

# Cellulosic Substrates for Removal of Pollutants from Aqueous Systems: A Review. Part 4. Dissolved Petrochemical Compounds

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Dissolved petroleum-based compounds, e.g. solvents, pesticides, and chemical reagents such as phenolic compounds, can pose significant hazards to the health of humans and ecosystems when they are released to the environment. This review article considers research progress related to the biosorption and removal of such contaminants from water using cellulose-derived materials. The fact that cellulosic materials show promise in removing such sparingly soluble materials from water lends support to a hypothesis that lignocellulosic materials can be broad-spectrum adsorbents. Also, the hydrophobic character and sorption capabilities can be increased through thermal treatment and the preparation of activated carbons. As shown in many studies, the efficiency of uptake of various petrochemical products from water also can be increased by chemical treatments of the adsorbent. It appears that more widespread adoption of biosorption as a means of removing petroleum-based products from water has been limited by concerns about the used, loaded biosorbent. Disposal or regeneration options that need to be considered more in future research include enzymatic and biological treatments, taking advantage of the fact that the biosorbent material is able to collect, immobilize, and concentrate various contaminants in forms that are suited for a number of packed bed or batch-type degradative treatment systems.

*Keywords:* Cellulose; Biomass; Biosorption; Remediation; Pollutants; Adsorption; Petroleum; Organic chemicals; Solvents; Pesticides; Wastewater treatment

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## INTRODUCTION

The water-soluble components of various petrochemical products, such as pesticides, solvents, plasticizers, and pharmaceuticals, pose hazards to people and to nature (Keith and Telliard 1979). The toxic nature of many petroleum-derived organic compounds has been well documented (Augulyte *et al.* 2008). Substances capable of disrupting the endocrine systems of people and animals are of particular concern (Sethunathan *et al.* 2004; Yu *et al.* 2008; Kumar *et al.* 2009a; Rossner *et al.* 2009; Chang *et al.* 2012; Jung *et al.* 2013; Ye *et al.* 2013; Soni and Padmaja 2014). Phenolic compounds, despite their limited aqueous solubility, are serious water pollutants, especially in the case of chlorinated phenolics (Igbinosa *et al.* 2013; Tsai 2013).

Alternative measures for removal of organic pollutants from water solution have been reviewed (Franklin 1991; Dvorak *et al.* 1993; Droste 1997; Özbelge *et al.* 2002; Demirev 2008; Thuy *et al.* 2008; Musteret *et al.* 2010; Pratarn *et al.* 2011; Margot *et al.* 2013). In particular, conventional wastewater treatment, using either activated sludge or various types of bioreactors, can induce biodegradation of many petrochemical products, at least in part (Juhász and Naidu 2000a; Farhadian *et al.* 2008; Marin *et al.* 2010; Kwon *et al.* 2011; Al-Khalid and El-Naas 2012; Krastanov *et al.* 2013; Niti *et al.* 2013).

Adsorption onto suspended particles has been proposed for many years as a promising route to remove petrochemical pollutants from dilute aqueous solutions (Morris and Weber 1962; Weber and Morris 1963). The general topic of biosorption also has been reviewed (Mattson and Mark 1971; Dobbs and Cohen 1980; Perrich 1981; Pollard *et al.* 1992; Vrana *et al.* 1998; Moreno-Castilla 2004; Aksu 2005; Dąbrowski *et al.* 2005; Mathialagan and Viraraghavan 2008; Gadd 2009; Lin and Juang 2009; Bhatnagar *et al.* 2010; Capasso and De Martino 2010; Zolgharnein *et al.* 2011; Delgado *et al.* 2012; Julinová and Slavík 2012; Pintor *et al.* 2012; Gupta and Saleh 2013; Liu *et al.* 2013; Michalak *et al.* 2013; Fomina and Gadd 2014). In the present discussion the term “biosorption” will be taken to include adsorption of pollutants on any sorbent material derived from plant matter. Activated carbons will be included, with emphasis placed on such products prepared from cellulosic raw materials. A recent article by Chowdhury *et al.* (2013) provides a thorough review and discussion of carbonization and carbon activation procedures, making it unnecessary to cover those aspects in as great detail in the present article. This article focuses on progress that has been made in the use of lignocellulosic materials, as well as its derivative products, for the removal of solubilized petrochemical products from water.

A subtheme of this article will be the extent to which cellulose-derived products can act as broad-spectrum absorbents. The earlier review articles in this series also showed that cellulose-based materials can be effective for the removal of heavy metals, dyes, and liquid or emulsified oils from water (Hubbe *et al.* 2011, 2012, 2013). It is notable that cellulosic products can be effective for the remediation of aqueous spills of oil-like substances, a capability that is not obvious based on the hydrophilic nature of the sugar units that make up cellulose. The scope of the third of the listed review articles was intentionally incomplete, since it did not deal with uptake of the dissolved portions of those oils. Thus, the present article completes the analysis for petroleum-derived products as a whole. Also it should be noted that, strictly speaking, the dyes reviewed in Part 2 of the

series can be considered as petrochemical products. So there will naturally be frequent references to aspects already covered in Part 2 (Hubbe *et al.* 2012).

The motivation to seek broad-spectrum absorbency stems from the nature of pollution. Only seldom does it happen that the material one wishes to remove from water is highly pure and highly characterized. It is far more common for polluted water to contain many substances that have not been identified. For instance, it is reasonable to expect that petrochemical-based compounds in samples of contaminated water may span the ranges between aliphatic and aromatic, hydrophilic to very sparingly soluble, and nonionic to highly charged, with huge ranges of molecular mass and volatility. In light of this diversity of potential sorbates, this review article will begin with consideration of diverse types of cellulosic materials – as well as transformed products such as torrefied wood and activated carbons – relative to the uptake of petroleum-based sorbates from water. As will be shown, while cellulosic biomass in general has a rather broad affinity for a wide range of petroleum-based substances, the affinity can be increased by various treatments. Also, one should not rule out the possible use of mixed sorbents, such as combinations of raw and torrefied biomass or sawdust together with fungal biomass, *etc.* Subsequent sections of the article will deal with attributes of common petroleum-derived contaminants that may be present in water samples, aspects of aqueous composition found to affect sorption, theoretical aspects, and life cycle issues.

## EXPERIMENTAL FINDINGS

### Overview

Research studies devoted to the removal of petrochemical-based substances from water by use of cellulose-derived sorbents have been both numerous and diverse, especially during the most recent decade. Key findings from articles considered in the present review are listed in Table A, which due to its length is placed in the Appendix. The table lists the information according to the categories of pollutant, adsorbent (including drying conditions and treatments), adsorption isotherms that best fit the data, adsorption capacities, the rate laws that best fit to data, and the main thermodynamic information – whether adsorption is exothermic or endothermic. Additional information of note appears in a column headed by “Key Findings”. The headings of the table correspond, in a rough sense, to the progression of topics in sections that follow.

### Sorbent Source Materials

Though just about every imaginable plant-based material has been studied relative to its potential use in adsorbing synthetic organic compounds, inspection of the second column in Table A reveals a preponderance of interest in the use of activated carbon sorbents. Results of such work will be summarized later in this section. The reason why activated carbon products receive so much attention can be attributed to a favorable combination of a hydrophobic nature, a high surface area, and a potentially favorable pore size distribution that can be changed depending on the conditions of preparation. But, as will be described, the conditions used in the preparation of activated carbons make such sorbents inherently more expensive than many other cellulosic materials due to the significant weight loss, energy usage, and chemical usage, especially in cases where the

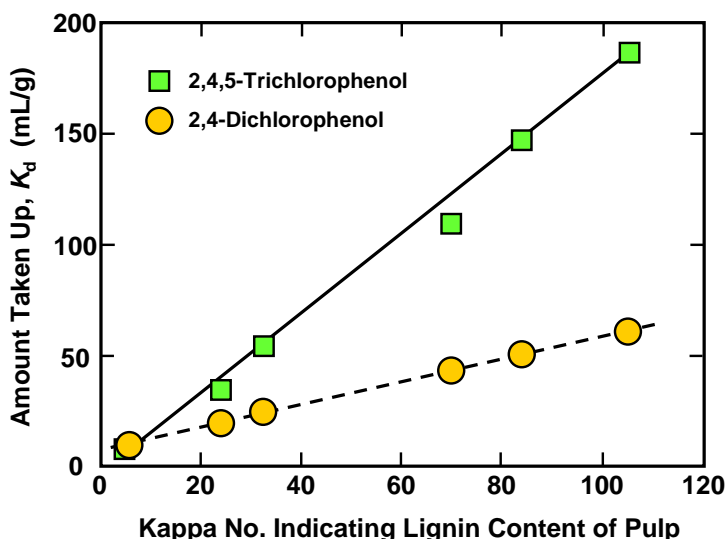
raw material can be obtained as an underutilized byproduct. So, one of the important questions to consider is whether and when it may make sense to favor the use of different kinds of sorbent materials.

### Wood

Adsorption tests of monoaromatic hydrocarbons onto unmodified softwood chips have been reported by Mackay and Gschwend (2000). Adsorption kinetics were found to be favorably affected by lignin content in the wood. But one of the key findings was that the rate of uptake into the wood was very slow, at least when it is utilized in the form of chips rather than fibers.

Huang *et al.* (2006) found that the adsorption characteristics of aspen wood fibers could be altered by bleaching and hydrolysis. An oxidative bleaching treatment removed the lignin, rendering the fibers more hydrophilic and more porous. Hydrolysis, with use of strong acid, mainly removed hemicellulose, thus yielding fibers having a higher aromatic character and lower polarity. In general, the bleaching treatment decreased the sorption capacity for phenanthrene and pyrene, whereas the hydrolysis treatment increased adsorption of both of the sparingly soluble compounds from aqueous solution.

The lignin component of wood is sometimes viewed as a potential sorbent for sparingly soluble organic pollutants due to its generally hydrophobic character. Lignin's capability for biosorption of phenolic substances was evaluated by Allen *et al.* (2005). Cuhha *et al.* (2010) showed that humins, which can be considered to be a product of the natural decomposition of lignin, can be used to adsorb trihalomethanes. Rodriguez-Cruz *et al.* (2007) compared the adsorption capacities for pesticides onto nine types of woods having a wide range of lignin content. There was a strong correlation between increasing lignin content and increasing sorption capacity. These results are consistent with the findings of Severtson and Banerjee (1996), as shown in Fig. 1.



**Fig. 1.** Dependency of two phenolic compounds onto cellulosic fibers vs. kappa number, which linearly correlates with lignin content. Data at near-zero kappa correspond to cotton. Other points were for softwood kraft fibers over a wide range of pulping and bleaching conditions. Uptake includes the amount contained in water solution that is within the pores and lumens of the fibers. Figure redrawn based on data from Severtson and Banerjee (1996).

Severtson and Banerjee (1996) studied sorption of chlorophenols onto pulped softwood kraft fibers having different extents of delignification. As indicated in Fig. 1, very little of the pollutants were adsorbed onto cotton cellulose (data points near to zero kappa number), whereas there was a very strong correlation between chlorophenol adsorption and the kappa number of the kraft pulps, the value of which is reflective of the relative amount of lignin remaining in the fiber.

Bark is another tree-derived material that has been considered as a potential biosorbent. Kumar and Min (2011a) and Kumar *et al.* (2012) showed that *Acacia leucocephala* bark could be used to remove chlorophenols. Related work with pine bark was reported by Kumar *et al.* (2014). Rotala *et al.* (2003) showed that pine bark can be used to remove the pesticides lindane and heptachlor from solution. A study by Li *et al.* (2010a) showed that pine bark contains substantial amounts of waxy substances, in addition to polysaccharides and lignin.

#### *Fungal sorbent material*

Relative to wood, fungal products have some key attributes that make them promising candidates for biosorption (Aksu 2005): The material tends to be less dense, making it reasonable to expect easier accessibility of various molecules into the fine pore structure. Also, much of the available fungal material is produced as a byproduct of other processes, such as fermentation, which are carried out at centralized locations. As shown by Kumar and Min (2011b), fungal biomass may contain significant amounts of nitrogen in the form of amines and amides; this is attributable to the presence of protein. Various researchers have evaluated fungal material relative to the uptake of phenols and other synthetic organic compounds from solution (Young and Banks 1998; Rao and Viraraghavan 2002; Denizli *et al.* 2005; Wu and Yu 2006b; Kumar *et al.* 2009b; Pernyeszi *et al.* 2009; Huang *et al.* 2010; Kumar and Min 2011b; Zhang *et al.* 2011c; Farkas *et al.* 2013). Rao and Viraraghavan (2002) found the highest uptake following pretreatment of *Aspergillus niger* with sulfuric acid.

#### *Bacterial sorbent material*

Ju *et al.* (1997) compared the adsorption of lindane onto Gram-positive and Gram-negative bacteria. Seo *et al.* (1997) explored the use of seeding micro-organisms into a membrane filtration system, in combination with activated carbon. The inoculated systems were found to be four times as effective in removing various hard-to-decompose organic substances from water. Though such studies involving bacteria have been relatively scarce, they can help contribute to an understanding of activated sludge systems for water treatment (Bell and Tsezos 1988; Aksu and Yener 1998, 2001; Vrana *et al.* 1998; Stringfellow and Alvarez-Cohen 1999; Aksu and Gönen 2004; Arslan and Dursun 2008; Augulyte *et al.* 2008; Pan *et al.* 2010; Yu and Hu 2011; Hai *et al.* 2012; Julinová and Slavík 2012; Khalaf *et al.* 2013). Thus, it is likely that biosorption can explain at least part of the ability of activated sludge-based wastewater treatment systems to remove various sparingly soluble pollutants from water (Tsezos and Bell 1988, 1989, 1991; Tsezos and Wang 1991).

*Living or dead microbial matter*

One key difference between a conventional activated sludge wastewater treatment system and most studies that have considered use of microbial matter as a biosorbent concerns whether the cells are alive or dead. Several studies have confronted this issue directly, using various means to optionally kill the microbes and find out any effects of such treatment on biosorption (Tsezos and Bell 1989). In some cases the extent of removal of pollutants from water was about the same, when comparing live vs. dead cells (Yan and Allen 1994; Johasz *et al.* 2002; Lei *et al.* 2002; Chen *et al.* 2010; Ding *et al.* 2013). There was evidence in some of the studies that adsorption onto microbial material may tend to protect the target compounds from enzyme-induced decomposition (Chen *et al.* 2010). On the other hand, increased adsorption of petrochemicals after autoclaving of microbial biomass to kill the cells has been observed in some cases (Wang and Grady 1994; Lang *et al.* 2009).

**Modification of Sorbent Materials**

Biomaterials have been modified physically, chemically, and by pyrolysis with an aim to determine the most suitable processing conditions to enhance adsorption capacities or other attributes of sorbents.

*Drying*

As was noted in earlier review articles concerned with biosorption of heavy metal ions and dyes (Hubbe *et al.* 2011, 2012), a majority of researchers have begun their analyses either with pre-dried cellulosic materials or by imposing a controlled drying step, using an oven (see Table A). Such procedures possibly can be justified in terms of better storage stability of the dried material. Also, the heat treatment can help to define the starting condition for testing. But the question of whether or not such drying may affect adsorption outcomes has been studied less frequently. Choi and Huber (2009) observed that the sorption of 1-methylcyclopropene from the atmosphere to fruit and vegetable materials was markedly reduced by drying. In that case, much of the adsorptive capability was restored when the material was rehydrated by a minute of wetting with distilled water. But other researchers have documented irreversible losses in the water-absorbing ability of cellulosic materials when they are dried (Stone and Scallan 1966; Weise 1998). The phenomenon is often called hornification (Jayme and Büttel 1968). Thus, there is a critical need for further research, especially in the case of phenolics and other potentially toxic organic compounds in water adsorbing onto plant material that is either never-dried, dried by exposure to different heating regimes, or rehydrated under different aqueous conditions (*e.g.* temperature, pH, and duration) to determine reversibility of the drying effect.

*Grinding of plant material*

A great many studies of biosorption begin with the grinding of dried plant-derived material into a fine powder (Table A). However, in the cited cases the authors generally did not run control tests to find out whether such grinding will affect biosorption results. Thus, again, there is a critical need for research in that area. The topic of “particle size” will be considered later.

### *Chemical pretreatments or extraction*

Certain studies have shown clear effects on biosorption after treating the plant-derived sorbent with acids, bases, or various solvents. For instance, Juhasz and Naidu (2006b) observed very significant increases in uptake of DDT and related pesticide compounds onto fungal mycelia after treatment with concentrated HCl. Chen *et al.* (2005) found that when plant cuticle material was solvent-fractionated into components having different polarity, such components differed greatly in their ability to take up polar and nonpolar organic compounds. Li *et al.* (2010a) showed that relatively severe extraction, using a Soxhlet device, as well as treatments with strong acid or base, were able to partition pine bark into components that differed greatly in their ability to adsorb polycyclic aromatic compounds. El-Sheikh *et al.* (2013) found surprisingly that washing of olive wood with various solvents made it more effective as an adsorbent for various phenolics. Presumably such an effect can be understood as a removal of hydrophobic materials from pore spaces, thereby making those spaces available for removal other hydrophobic substances from water. However, the cited observation can be considered surprising because one might expect that removal of hydrophobic components from lignocellulosic material would render it more hydrophilic and less oleophilic.

### *Chemical derivatization and grafting*

The adsorptive characteristics of plant-derived materials clearly can be changed by reactions that place new functional groups on the solid surfaces. Maurin *et al.* (1999) treated sawdust with fatty acids and demonstrated increased removal of fats from water. Vismara *et al.* (2009) and Sokker *et al.* (2009) grafted glycidyl methacrylate (GMA) onto cotton, which in its untreated state was ineffective for adsorption of phenol. The derivatized cotton, depending on the detailed structure of the functional groups, was highly effective as an adsorbent. Hsu and Pan (2007) and Hsu *et al.* (2009) showed that grafting of methacrylic acid onto rice husk greatly enhanced its ability to take up paraquat.

For high-end applications, such as purification of petrochemical compounds present in aqueous solution, it has been shown feasible to chemically “imprint” a polymeric adsorbent, using the target molecule as a template (Shaikh *et al.* 2012). The cited authors showed that such a system could be used to bind and enrich an endocrine disruptor molecule, thus amplifying and simplifying subsequent chromatographic analysis. Such a concept has potential to be incorporated into a system for biosorption of specific molecules, using cellulosic materials as a support.

### *Torrefaction of cellulosic matter*

The word torrefaction can be defined as the applications of mild thermal treatment in the range of about 200 to 300 °C in the partial or complete absence of oxygen (van der Stelt *et al.* 2011). Such treatment can significantly change the composition and behavior of woody material. Torrefaction has been shown to cause chemical changes due to the loss of volatile components and hemicelluloses. In addition, the changes in lignin structure (e.g. the amount of non-protonated carbon characterized by solid-state NMR) has been reported in this temperature range (Park *et al.* 2013). There has been a lot of attention directed to the topic of torrefaction in the most recent decade as a promising means to upgrade the energy-density and burning characteristics of pellets and briquettes (van der Stelt *et al.* 2011; Giudicianni *et al.* 2013; Ibrahim *et al.* 2013). But some other changes

brought about by torrefaction of wood suggest potential applications in the adsorption of oleophilic species from water. For example, various studies have shown that torrefaction tends to make the treated material more hydrophobic (Ibrahim *et al.* 2013). Penmetsa and Steele (2012) took this approach one step further by adding a binder, before torrefaction, such that the final product was sufficiently hydrophobic to resist moisture when shipped in open containers. In none of the cited studies was there any attempt to evaluate the uptake of petrochemicals from water; thus research in this area is critically needed.

#### *Biochars and carbonation*

The term “biochars” can denote a broad range of cellulose-derived products that have been pyrolyzed to various degrees sufficient to cause at least partial carbonation, *i.e.* the conversion of polysaccharides and/or lignin to such carbon species as graphite (Reed and Williams 2004; Anderson *et al.* 2013; Giudicianni *et al.* 2013). Rutherford *et al.* (2012) found that aliphatic components tended to be lost, leaving behind material enriched in aromatic content. Various studies have shown that biochars can be used as biosorbents to remove petrochemicals from water (Edgehill and Lu 1998; Jonkers and Koelmans 2002; James *et al.* 2005; Chen and Chen 2008, 2009; Zheng *et al.* 2010; Kong *et al.* 2011b; Ni *et al.* 2011; Ahmad *et al.* 2012, 2013; Chen *et al.* 2012b; Denyes *et al.* 2012; Mubarik *et al.* 2012; Das *et al.* 2013; Hao *et al.* 2013; Zheng *et al.* 2013; Mohan *et al.* 2014). Ahmad *et al.* (2012) attributed increased adsorption of trichloroethylene after pyrolysis to a combination of increased hydrophobicity and surface area. Also, the aromatic character of the surface tends to be increased (Hao *et al.* 2013). Karakoyun *et al.* (2011) showed that effective biosorption of organic contaminants could be achieved with a composite prepared from a hydrogel and biochar.

One of the potential advantages of biochars prepared under intermediate thermal conditions is that there might be a high diversity of surface sites. James *et al.* (2005) found that the heterogeneity of surface sites in biochar depends on both the starting material and the temperature of pyrolysis. Mohan *et al.* (2014), who reviewed the topic of adsorption of contaminants onto biochar, noted that such sorbents typically have much higher oxygen, hydrogen, and ash content in comparison to typical activated carbons. The cited article showed very wide ranges in the reported adsorption capacities of different biochars for a range of metal ions; presumably much of the differences might be attributable to differences in conditions of charring, *e.g.* temperature, time, and atmosphere. Biochars also have the potential for lower cost than the available activated carbons, though as Mohan *et al.* (2014) point out, such an advantage may slip away as soon as one attempts to upgrade the material to improve its adsorption capacity or other performance issues.

Biochars have been often suggested as playing a key role in carbon sequestration, since biochar added to soils can be expected to persist for many decades (Rutherford *et al.* 2012). But in addition, such biochar can be expected to play a role in binding sparingly soluble organic contaminants that may be present in the soil (Lou *et al.* 2011; Deneyes *et al.* 2012; Hao *et al.* 2013; Li *et al.* 2013a). One potentially problematic aspect of biochar addition to soils is the fact that some polycyclic aromatic hydrocarbons (PACs), which can be considered as pollutants, may come from the biochar itself (Fabbri *et al.* 2013; Quilliam *et al.* 2013). A slow pyrolysis process was recommended by Fabbri *et al.* (2013) in order to minimize the level of the PACs that originate from the biomass or from its conversion into char.



### *Activation of carbon*

The term “activated carbon” implies a material that has been pyrolyzed under conditions leading to very high internal surface area. Though substantial quantities of carbon products are prepared from fossil resources such as coal (Dumanli and Windle 2012), there is increasing interest in preparation of activated carbons from a variety of biomass sources (Choudhury *et al.* 2013). In particular, coconut shell is a major source for the production of activated carbons. Activated carbon products have a complex, interconnecting pore nanostructure that can be influenced by the treatment conditions. The subject of activated carbons, including strategies and theories related to their optimization, has been described in greater detail elsewhere (Dias *et al.* 2007; Suhas *et al.* 2007; Chowdhury *et al.* 2013). Briefly stated, the production of activated carbons typically entails treatment at temperatures in the range of 600 to 1200 °C. But mere carbonizing of the plant-derived material in an oxygen-poor environment generally would not succeed in production of a high surface area material with a favorable balance between micropores (less than 2 nm) and mesopores (2 to 50 nm) (Rouquerol *et al.* 1994). One approach to achieving such objectives entails adding such reagents as KOH, NaOH, H<sub>3</sub>PO<sub>4</sub>, or H<sub>2</sub>SO<sub>4</sub> before the final stage of pyrolysis (see Table A). Another approach is to treat the system with steam during pyrolysis (see later).

Various studies have shown favorable effects of activation treatments on the uptake of petrochemicals from aqueous systems. Such studies can be identified in Table A by the letters “AC” (for “activated carbon”) in the third column. As is evident from many of the values shown in the 6<sup>th</sup> column, activated carbons typically exhibit high adsorption capacities in comparison to most other types of sorbents.

Because of the profoundness of the changes brought about by pyrolysis and activation, it appears that details of the starting cellulosic material can become unimportant. For example, Klasson *et al.* (2010) found no significant differences between activated carbons prepared from different batches of nut shells. As long as the material was relatively uniform it was possible to prepare activated carbon of high quality and effectiveness. More prominent effects related to the source material were reported by Yeganeh *et al.* (2006), who compared a much more diverse set of biomass types.

### *Activating compound*

The performance of carbon-based absorbents can be greatly enhanced by treatment of the carbon with certain chemicals, either initially or before a final activation stage. Potassium hydroxide is one of the most widely studied activating agents (Wu *et al.* 2005; Radhika and Palanivelu 2006; Tan *et al.* 2008; Kilic *et al.* 2011; Wu *et al.* 2011, 2012b; Kong *et al.* 2012). Radhika and Palanivelu (2006) found that KOH-activated carbon outperformed products that they prepared from five other activating systems relative to sorption of chlorophenol. Wu and Tseng (2006) and Tan *et al.* (2008) described the action of KOH as “etching”, a treatment that renders the carbon susceptible to the generation of pores. The cited authors showed that a combination of KOH activation followed by pyrolytic treatment with CO<sub>2</sub> had a promising effect on phenol sorption. Chen *et al.* (2012a) employed the unique approach; instead of adding KOH they selected a biomass source inherently rich in potassium. After pyrolysis the material had a well-developed mesoporous structure and exhibited a high ability to adsorb phenol from water.

Phosphoric acid is another of the most widely reported activating compounds for preparation of activated carbons (Toles *et al.* 1997, 1998; Daifullah and Girgis 1998, 2003; Kennedy *et al.* 2007; Aber *et al.* 2009; Anirudhan *et al.* 2009; Klasson *et al.* 2009; Bello-Huitle *et al.* 2010; Timur *et al.* 2010; Moreno-Pirajan *et al.* 2011). Kennedy *et al.* (2007) found that a two-stage process, with an initial carbonation stage followed by addition of the activating agent ( $\text{H}_3\text{PO}_4$ ) and further pyrolysis, yielded a favorable combination of micropores and mesopores – offering both high sorption capacity and relatively quick equilibration.

Other activating agents that have been considered to improve the adsorption of petrochemicals from water include zinc chloride (Mohanty *et al.* 2005; Nath *et al.* 2008; Subha and Namasivayam 2009, 2010; Timur *et al.* 2010; Aravindhnan *et al.* 2011), carbon dioxide (Ferro-Garcia *et al.* 1996; Toles *et al.* 1997; Teng and Hsieh 1999; Wu and Tseng 2006; Hameed *et al.* 2009; Zhong *et al.* 2012), sodium hydroxide (Tseng *et al.* 2010, 2011; Fierro *et al.* 2008), potassium carbonate (Mestre *et al.* 2007; Kilic *et al.* 2011), and nitric acid (Nabais *et al.* 2009; Mourão *et al.* 2011). Sulfuric acid, when used as an activating agent, has been said to help dehydrate the raw material and to aid in formation of a porous texture (Cuerda-Correa *et al.* 2006). Iniesta *et al.* (2001) reported that sulfuric acid also can result in lower ash content. Because some of the ash may have a catalytic effect, the removal of mineral content may affect char reactivity.

#### *Steam activation*

Several investigators have reported that steam activation of carbon can be effective to increase the sorption capacity for hydrophobic organic compounds (Ng *et al.* 2000; Juang *et al.* 2001; Galiatsatou *et al.* 2002; Vinod and Anirudhan 2002; Tseng *et al.* 2003; Reed and Williams 2004; Kumar *et al.* 2006; Mestre *et al.* 2007; Klasson *et al.* 2009, 2010; Anderson *et al.* 2013; Bai *et al.* 2013). Ahmedna *et al.* (2004) found that steam-activated carbon outperformed acid-activated carbon for the sorption of chlorination byproducts from drinking water. Bansode *et al.* (2003) likewise found that activation with either steam or  $\text{CO}_2$  was more effective than other activation systems considered for enhancing the uptake of volatile organic compounds.

#### *Post-treatments of activated carbons*

Various authors have described enhancement procedures for activated carbons that might be called “post-treatments”. It appears that the general goal of such treatments has been to modify the nature of surface sites on the material, while attempting to avoid too much damage to the pore size distribution and surface area attributes achieved in previous steps. Alvarez *et al.* (2005) treated activated carbons with ozone and showed evidence of an increased level of acidic functional groups on the surface. Nevskaya and Guerrero-Ruiz (2001) showed that post-treatment with nitric acid was another way to increase the content of oxygen-containing groups at the surface of activated carbon. Qu *et al.* (2013) showed that by post-treatment with nitrogen plasma it was possible to reduce the frequency of oxygen-containing groups in activated carbon, together with a loss of surface area; by contrast, treatment with an oxygen plasma increased both oxygen content and specific surface area. Mahajan *et al.* (1980) had shown earlier that post-treatment with a nitrogen atmosphere increased the adsorption capacity for phenol. Leng and Pinto (1997) considered the effects of oxygenation, de-oxygenation, and HCl-washing. Mild oxidation

showed promise for extending the service life of regenerated activated carbon. Quinlivan *et al.* (2005) showed that the surface chemistry of active carbon could be modified by acid washing, oxidation, hydrogen treatment, or ammonia treatment, and such changes affected the adsorption of methyl tetra-butyl ether and trichloroethene.

Post-treatment can be used as a way to change the surface composition and make an activated carbon product more effective for specific applications. Thus, Radovic *et al.* (1997) found that an increase in acidic groups on the sorbent surface increased the uptake of aniline, a basic material, whereas an increase in graphene content favored uptake of the neutral, hydrophobic compound nitrobenzene. Stavropoulos *et al.* (2008) post-treated active carbon to introduce acidic or basic properties using partial oxygen gasification, nitric acid, or urea followed by pyrolysis. The urea treatment resulted in higher nitrogen content of the sorbent and led to the greatest increase in uptake of phenol. Tessmer *et al.* (1997) observed that adsorption of phenolic compounds was favored by carrying out the final pyrolysis in the absence of oxygen, thus lowering the content of acidic groups at the surface of the sorbent.

### Attributes of Sorbent Materials

The goal of this section is to discuss evidence, provided in the literature, to support the hypothesis that the ability of cellulose-based materials to take up sparingly soluble synthetic organic materials from water is somehow related to either the physical structure or the chemical nature of the solid surfaces. Attributes related to physical structure will be considered first.

#### *Particle size of the cellulose-based sorbent*

If one starts with a simple model in which sorbate molecules are envisioned as adsorbing mainly onto outer surfaces of the sorbent material, then it would follow that adsorption capacity, or at least the initial rate of uptake, ought to increase with decreasing particle size. A number of publications that have provided information that permit some testing of such idealized models will be considered here.

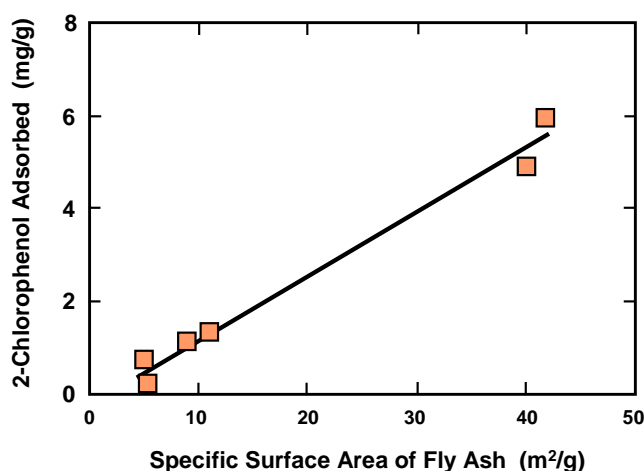
Several studies reported strongly rising adsorption capability with decreasing particle size of the adsorbent (Munaf *et al.* 1997; Brás *et al.* 1999, 2005; Garcia-Mendieta *et al.* 2003; Boussahel *et al.* 2009). For adsorption of DDT from aqueous solution onto sawdust or cork powders, Boussahel *et al.* (2009) observed a five to ten times higher initial rate of adsorption onto 0.2 mm particles compared to 0.5 mm particles. Brás *et al.* (1999, 2005) found a similar relationship for the adsorption capacity of organochlorine compounds on pine bark. One common feature that may help account for the findings cited above is that the mentioned sorbent materials tended to be relatively dense or limited in porosity.

Some other studies have shown little or no relationship between adsorption capacities and particle size of the adsorbent (Garcia-Mendieta *et al.* 2003). Presumably in such cases the diffusion of the adsorbate was sufficiently rapid that particle size did not matter very much, at least within the time scales considered in the cited studies. This is especially true in the case of activated carbons, which are generally known for their high porosity. Also, many activated carbons have been optimized to have a high content of mesopores, which are large enough to promote relatively rapid transport of adsorbates into interior spaces. Koumanova *et al.* (2003) found higher initial adsorption rates onto smaller

particles even in the case activated carbon, an effect that might be at least partly attributed to relatively slow diffusion into the interior of particles. Zheng *et al.* (2010) found that less time was required to reach equilibrium adsorption of triazine pesticides onto smaller particles of biochar. Leyva-Ramos *et al.* (1999) reported increased adsorption capacity of smaller activated carbon particles when adsorbing phenol from aqueous solution; no effect of particle size was found when the adsorption was from cyclohexane solution. Kao *et al.* (2000) surprisingly observed higher adsorption capacity for chlorophenols in the case of larger fly ash particles than smaller particles. This unusual effect was attributed to a different chemical composition of the bigger particles compared to the smaller ones. The bigger particles were found to have a higher carbon content, which apparently contributed to a higher sorption capacity.

#### *Surface area of the cellulose-based sorbent*

Taking a somewhat more sophisticated approach, several studies have attempted to correlate adsorption capacities to the measured surface areas of sorbent materials. Positive correlations between the surfaces areas (usually determined by nitrogen adsorption at very low temperature in a near-vacuum) and the amount of petrochemical adsorbed from aqueous solution have been reported by several groups (Moreno-Castilla *et al.* 1995b; Teng and Hseigh 1999; Kao *et al.* 2000; Hao *et al.* 2013). Figure 2 shows results obtained by Kao *et al.* (2000) for adsorption of 2-chlorophenol onto fly ash samples having different specific surface area. Further demonstration of the importance of porosity has been evident in the unusually low sorption capacities sometimes reported for adsorption onto cork, which tends to be rather impervious (Domingues *et al.* 2005).



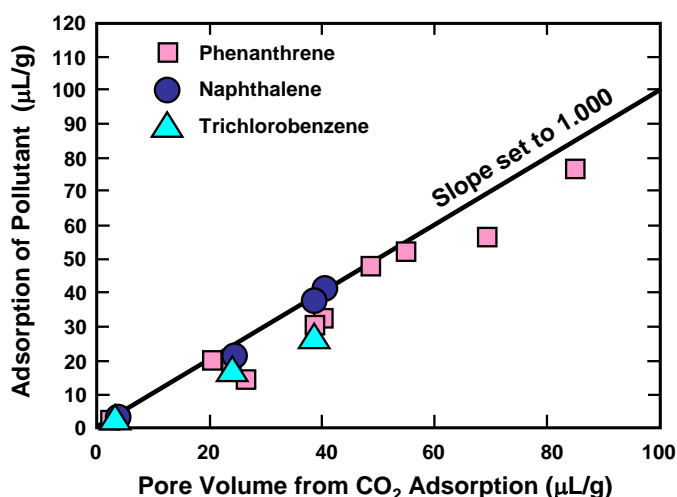
**Fig. 2.** Relationship between adsorbed amount of 2-chlorophenol and the specific surface area of fly ash fractions. Data from Kao *et al.* (2000) were replotted.

Not all publications support a hypothesis that adsorption increases with increasing surface area. For instance, Brás *et al.* (2004) reported that pine bark is “an encouraging sorbent for cheap water remediation solutions” despite the fact that it was found to have a low specific surface area. Unpublished findings by the authors suggest that although the adsorbed amount generally may increase with increasing surface area, the experimental

results can be highly dependent on experimental conditions such as the manner of washing and the flow rate.

### Pore volume

Chiu *et al.* (2003) found that it was the pore volume of the micropore structure, rather than the surface area, that seemed to control the sorption of toluene vapor onto natural organic materials. Pore volumes based on analysis of nitrogen adsorption in a near-vacuum at very cold temperature correlated well with the uptake of the toluene vapor at ambient temperature. Likewise, Ran *et al.* (2013) concluded that it was the void volume rather than the surface area that determined the amounts of nonpolar organic contaminants adsorbing on natural organic solids. Their data are shown replotted in Fig. 3. Note that the plotted line represents a slope of exactly one (unlike the lines plotted in the original publication). It is remarkable how closely the adsorption of the pollutants agreed with the pore volume determined separately by adsorption of carbon dioxide. Garcia-Mendieta *et al.* (2003) reached similar conclusions when comparing adsorption of phenols onto activated carbon products. Rivera-Utrilla *et al.* (1991) found that the pore volume accessible to water was a good indicator of adsorption capacity of activated carbons for removal of chlorophenols from water.



**Fig. 3.** Adsorption of phenanthrene, naphthalene, and trichlorobenzene onto eleven samples of natural organic matter relative to the pore volume determined by carbon dioxide adsorption. Data from Ran *et al.* (2013) replotted.

### Pore size

Several research teams concluded that it is not the pore volume *per se* that governs the adsorption capacity of activated carbon products, but rather the net volume of pores in the micropore range (formally less than 2 nm in diameter). Juang *et al.* (2001) found a strong correlation between the microporosity of activated carbons and their sorption capacities for phenols. Fierro *et al.* (2008) found good agreement between the net volume of micropores in activated carbons and the adsorption of phenol, with additional influences due to chemical factors. Karanfil and Dastgheib (2004) concluded that the pore volume

associated with micropores governed the capacity of granulated carbon for adsorption of trichloroethylene from water. Kumagai *et al.* (2009) reached a similar conclusion for adsorption of dibenzothiophenes from kerosene onto activated carbons; the mesopores were regarded by those authors as mainly a way to conduct the sorbate to the smallest category of pores. Presumably the adsorbate has a strong tendency to completely fill pores if they are smaller than a critical dimension, whereas adsorbate merely coats the surface of larger pores.

#### *Pore size distribution*

More complex relationships have been reported by investigators who considered somewhat larger sorbate molecules (Li *et al.* 2002; Newcombe *et al.* 2002a; Karanfil *et al.* 2006; Yang *et al.* 2006a,b). In principle, for each size of sorbate molecule, there must be an optimal size of pore that is large enough to accommodate that sorbate with high affinity. Thus, Hsieh and Teng (2000) proposed that sorbents having a range of pore size will have a consequent range of adsorption energies, such that smaller pores, still able to accommodate the sorbate, exhibit higher energies of adsorption. If pores are too small, then either the adsorption will be unfavored (due to restricted molecular motions) or impossible (because the sorbate molecule simply does not fit). In consideration of such factors, Quilivan *et al.* (2005) proposed an ideal pore size of 1.5 times the kinetic diameter of the target adsorbate.

Micropores, *i.e.* those having diameter below 2 nm, often account for the largest component of surface area in activated carbon products (Urano *et al.* 1991; Aber *et al.* 2009). The following studies reported cases in which the finest pores were too small to accommodate one or more adsorbates (Li *et al.* 2002; Ali *et al.* 2012). Furthermore, very narrow pores are more prone to clogging (Amstaetter *et al.* 2012). However, in other cases, the adsorption of the target pollutant was increased by increased microporosity of activated carbon (Bai *et al.* 2013). Galiatsatou *et al.* (2002) found a correlation between mesoporosity and adsorption of phenols, whereas other sorbates appeared to be mainly influenced by the extent of microporosity. Ji *et al.* (2010) found evidence that humic acid molecules, which are relatively large, may fail to fill micropores in activated carbon; such exclusion was proposed as a mechanism to account for the non-competition between the humic acids and tetracycline on graphite and carbon nanotubes. Martín-Gullón and Font (2001) attributed high removal of pesticide from water to the presence of “low size mesopores”, *i.e.* a class of pores that provided a good balance between rapid diffusion and fairly high surface area.

Caturla *et al.* (1988) proposed that if the pore size distribution of activated carbon is sufficiently broad, thus presenting few barriers to adsorption, then the adsorption process ought to become more influenced by factors such as chemical affinity. Indeed, Seredych and Badosz (2011) documented cases in which sulfur-to-sulfur affinity was strong enough to promote significant adsorption within mesopores in addition to the micropores. Chen *et al.* (2005, 2008) proposed that adsorption can be “porosity-selective” within a certain size range of pores, whereas adsorption can be “polarity-selective” in some other cases. It is worth noting that the broad pore-size distributions present in many well-designed activated carbon products are in contrast to the extremely uniform microporosity inherent in zeolite materials (Rossner *et al.* 2009). Sakoda *et al.* (1987) argued that a combination of

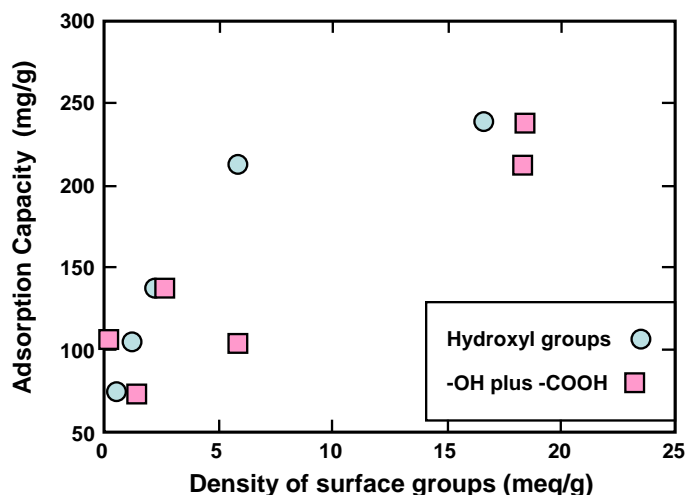
microporosity (offering a high surface area) and mesoporosity (offering a shorter diffusion path and more rapid equilibration) is likely to give the best overall performance.

#### *Sorbent chemical composition*

The sorbent's chemical composition, and in particular the chemistry of the surface, can be expected to play a major role in determining the ability to bind various species from solution. For instance it makes sense to expect that cork, which has a chemical composition quite different from most other plant materials (Olivella *et al.* 2013), might have a quite different affinity for hydrocarbons. The suberin component, which is generally understood to provide the impervious nature of cork, is not found in most other plant materials. However, in the cited study, the content of aromatic groups in the cork had a bigger contribution to adsorption of polycyclic aromatic hydrocarbons.

#### *Oxygen content of the surface*

Several studies have considered the extent to which the oxygen content of the surface of cellulose-based sorbents – especially activated carbon products – has an influence on the uptake of various petrochemical compounds from solution (Franz *et al.* 2000; Galiatsatou *et al.* 2002; Alvarez *et al.* 2005; László *et al.* 2006; Fierro *et al.* 2008). In many such studies, the adsorbed amounts were found to decrease as the oxygen content of the adsorbent surfaces became higher (Coughlin *et al.* 1968; Mahajan *et al.* 1980; Tessmer *et al.* 1997; Franz *et al.* 2000; Nevskaia and Guerrero-Ruiz 2001; Li *et al.* 2002; Salame and Badosz 2003; Dąbrowski *et al.* 2005; Mestre *et al.* 2007; Okawa *et al.* 2007; Stavropoulos *et al.* 2008; Blanco-Martínez *et al.* 2009; Leyva-Ramos *et al.* 2009b; Kong *et al.* 2011a; Sun *et al.* 2012b; Das *et al.* 2013; Olivella *et al.* 2013).



**Fig. 4.** Phenol adsorption onto activated carbons as a function of the amounts of oxygen-containing groups (hydroxyls or the sum of hydroxyls and carboxyls). Data from Fierro *et al.* (2008) were replotted.

In other cases there was little observed effect when comparing adsorbents having different levels of surface oxygen groups (Coughlin and Ezra 1968; Haydar *et al.* 2003). Higher uptake with increasing oxygen content of the adsorbent was observed for the

adsorption of ethanol (Bai *et al.* 2013), phenol (Leng and Pinto 1997; Podkościelny *et al.* 2003; Fierro *et al.* 2008), polyaromatic compounds (Gotovac *et al.* 2007b), trihalomethanes (Lu *et al.* 2005), and fluorinated herbicides (Sun *et al.* 2011a). Figure 4 shows data from Fierro *et al.* (2008), which suggests a positive influence of oxygen-containing groups on the adsorption of phenol onto activated carbons that had been modified in different ways.

One aspect that needs to be borne in mind, when considering such findings, is that treatments capable of changing the oxygen content of the surface of activated carbons can be expected to also affect the surface area and distribution of pore sizes. Thus, Teng and Hsieh (1999) attributed the greater adsorption of phenol onto carbons with higher oxygen content to the larger surface areas of such adsorbents. Dąbrowski *et al.* (2005) proposed, based on their study of the literature, that phenols mainly are bound to oxygen-free sites at the edges of graphene sheets in the carbonized material.

#### *Nitrogen content of the surface*

Stavropoulos *et al.* (2008) correlated the presence of nitrogen at activated carbon surfaces with increased affinity for phenol. Likewise, Wu *et al.* (2012b) prepared activated carbon with a high nitrogen content and found a high capacity for phenol adsorption. Sun *et al.* (2012b) found a positive relationship between N content and adsorption of phthalic esters; the effects was attributed to the hydrogen bonding capability of the nitrogen-containing groups. Zhang *et al.* (2013) found a similar relationship in the case of phenanthrene. Yaghmaeian *et al.* (2014) found that activation of carbon in the presence of NH<sub>4</sub>Cl yielded more effective uptake of amoxicillin, presumably due to the interaction between the carboxylate group of the antibiotic and the basic nitrogens ending up on the activated carbon.

But increased nitrogen content may not be a suitable approach for sorption of more hydrophobic species. As in the case of oxygen, the presence of nitrogen at the surface of activated carbon contributes to a hydrophilic character; with this in mind, Li *et al.* (2002) suggested that nitrogen content should be kept low when designing activated carbon products for adsorption of organic contaminants.

#### *Polar character of the absorbent surface*

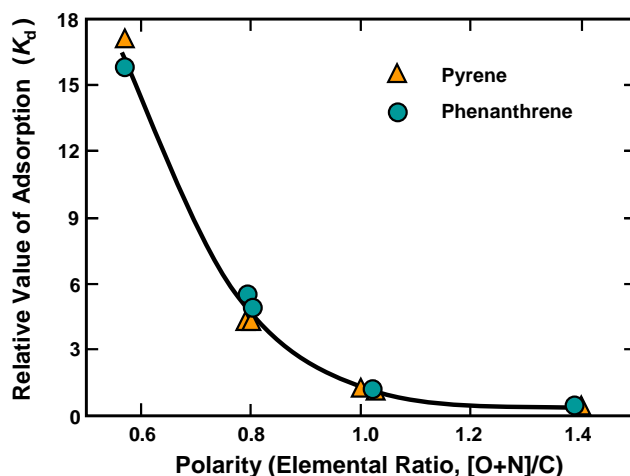
Several authors have postulated that the polar character of sites at the absorbent surface contribute to adsorption, especially in the case of phenolic adsorbates (Aksu and Yener 2001; Chen *et al.* 2005; Akhtar *et al.* 2006). Other researchers have found higher adsorption of nonpolar sorbate species when the adsorbent surface was less polar (Huang *et al.* 2006; Chen *et al.* 2008; Olivella *et al.* 2013; Zhang *et al.* 2013). Haghseresht *et al.* (2002b) proposed that different mechanisms can be important for adsorption when one compares effects of hydrophilic vs. hydrophobic types of activated carbons.

Though it might be argued the “hydrophobic” is merely another way of saying “non-polar,” several authors have suggested the content of specific hydrophobic compounds already present in adsorbents can account for the differing abilities of activated carbon surfaces to take up various petrochemical compounds (Li *et al.* 2002; Karanfil and Dastgheib 2004; Quinlivan *et al.* 2005; Li *et al.* 2010a; Hao *et al.* 2013). Thus, Barbour *et al.* (2005) found that lipids, a hydrophobic component of plant tissues, were primarily responsible for uptake of aromatic organic pollutants from water. Likewise, Boucher *et al.* (2007) found that residual oils in press-cake from oilseed processing had a high affinity for



adsorption of the pesticides carbaryl, atrazine, and parathion. Chen and Li (2007) found that removal of wax from plant cuticles made them less effective for the adsorption of naphthol. Lin *et al.* (2007) found that the adsorption of hydrophobic organic compounds onto tea leaf powders increased with the content of aliphatic carbons; Sun *et al.* (2012a) reached similar conclusions in the case of herbicide adsorption by biochars. Likewise, Salloum *et al.* (2002) found that the aliphatic carbons in organic matter were largely responsible for adsorption of phenanthrene. Chen and Schnoor (2009) found that removal of the hydrophobic suberin from root tissue rendered the adsorbent material less effective for phenanthrene. Similarly, Ghosh *et al.* (2009) found that removal of lipids from *Rhizopus oryzae* biomass decreased the ability of the adsorbent to take up lindane. Choi and Huber (2009) attributed higher adsorption of 1-methylcyclopropene to certain plant materials to the greater hydrophobicity of lignin. Li *et al.* (2012) correlated the adsorption of chlorophenols onto fruit cuticles and potato periderm fractions to the content of hydrophobic components such as waxes and cutin.

The influence of the polarity of the sorbate material is illustrated in Fig. 5, which is based on data from Li *et al.* (2010b). Different fractions of material derived from pine bark were used to adsorb pyrene and phenanthrene from aqueous solution. The uptake showed a very high dependency on the ratio of the sum of the nitrogen and oxygen elements to the amount of carbon element. As shown, each of the target chemicals was adsorbed at much higher efficiency if the polarity was very low, *i.e.* as little as possible of nitrogen and oxygen in the component obtained from pine bark.



**Fig. 5.** Dependency of adsorption capacity of different extracted components from pine bark on the [O + N]/C ratio (Figure replotted from the data of Li *et al.* 2010b).

#### *Acid/base character of the absorbent surface*

Some of the effects just described, involving relative contents of oxygen and nitrogen at adsorbent surfaces, might be explained in terms of the acidic or basic character of the surfaces. That is because oxygen at a carbon-rich surface is often in the form of carboxylic acids, whereas nitrogen is often present as basic amine groups. The following studies provided support for the idea that acidic or basic groups on an adsorbent surface were favorable for adsorption of certain species from solution (Fierro *et al.* 2008; Stavropoulos *et al.* 2008). Similarly, Mattson *et al.* (1969) used the term “charge-transfer”

to explain the preferential adsorption of adsorbate molecules based on the electron-density of surface sites. However, given the importance of acidic or basic character in many branches of technology, it is striking how few studies have emphasized such issues among those surveyed in the present work.

#### *Diversity of adsorption sites*

In view of the fact that most contaminated waters contain a wide variety of pollutants, there may be a preference for “broad-spectrum” adsorbents having the capability of removing many contrasting compounds. Heterogeneity of adsorption sites has been noted as an important attribute (Snoeyink *et al.* 1969; Podkościelny *et al.* 2003; Pan and Xing 2008; Rossner *et al.* 2009; Sun *et al.* 2011b). One of the ways in which a substrate can be heterogeneous can involve ionically charged groups (Müller *et al.* 1980). Thus, László *et al.* (2003, 2006) and Dąbrowski *et al.* (2005) point out that the charge heterogeneity of a sorbent, which might be called its amphoteric character, tends to be greater at intermediate pH values where both amines and carboxylic acids can be present in their charged forms. Sun *et al.* (2011b) suggested that hydrothermal biochars may be superior to thermally-produced biochars in terms of the chemical diversity of the surface sites. Another aspect of heterogeneity, as described by Hseigh and Teng (2000) and Rossner *et al.* (2009), is due to the different sizes of pores, offering capability to take up a spectrum of different adsorbates having different attributes (see next section).

#### **Attributes of the Sorbate**

Petrochemical compounds present in water can vary over large ranges with respect to many attributes, including molecular weight (*i.e.* molecular size), shape, solubility in water (or polarity), aromatic character, and ionic charge. Specific functional groups might also be important in some cases. This section considers published findings that help to address the hypothesis that such differences in the sorbate can have an important influence on their removal from aqueous solution by adsorption.

#### *Molecular weight of the adsorbate*

The importance of molecular size of the sorbate molecules already was mentioned in the earlier discussion of findings related to the pore size distributions of adsorbents. Thus, studies have identified cases in which the dissolved compounds were too large to be efficiently adsorbed within micropores (Yang *et al.* 2006a,b; Ali *et al.* 2012). Correa (2009) explained similar findings based on kinetics, noting that increasing numbers of chlorine substituent atoms imply larger size of chlorophenol molecules; the larger molecules can be expected to exhibit slower rates of diffusion into the fine pore structure of a cellulose-based adsorbent. As was noted earlier, one can expect there to be an optimum pore size, estimated to be 1.3 to 1.8 times larger than the kinetic diameter of the sorbate, which will give the greatest uptake (Li *et al.* 2002). In principle the free energy of adsorption will be maximized when there is a suitable balance between such factors as (a) favorable surface interactions (enthalpy term), and (b) sufficient space for the molecules to move around (entropy term) (Maginn *et al.* 1995; Jaroniec and Choma 1997; Adolphs 2007). In other cases the size of a sorbate molecule appears to play an underlying role relative to its affinity to the adsorbent surface (Nouri *et al.* 2002a). Higher molecular mass often implies a greater tendency to adsorb (Haghseresht *et al.* 2002a; Choi *et al.* 2003;

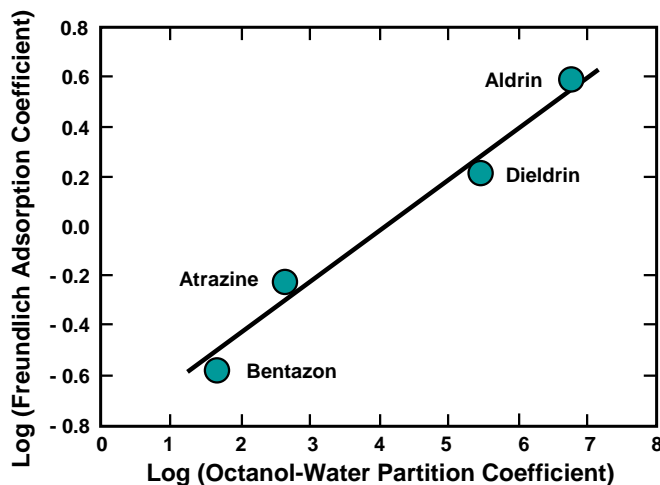
Boving and Zhang 2004; Gao and Wang 2007; Hansen *et al.* 2010; Julinová and Slavík 2012; Kusmierek *et al.* 2013). Larger molecules in general would be expected to have higher free energy of adsorption, per unit molecule.

#### *Molecular shape of the adsorbate molecule*

The topic of molecular shape seems to have been considered in only a few cases. Thus, Karanfil and Dastgheib (2004) found that trichloroethylene molecules were able to access the interior regions of microporous activated carbons; this ability was attributed to a flat molecular shape. There was no demonstration, however, of whether different results would be obtained with a different molecular shape, all things being equal. Likewise, Jonker and Koelmans (2002) observed preferential adsorption of planar molecules. The work of Ozdemir *et al.* (2012) includes a suggestion that maybe some of the observed differences in adsorption behavior of chlorophenoxy acid derivatives might be related to the presence or absence of chirality. Such ideas might be the subject of future studies, especially if the concepts can be backed up by molecular dynamics simulations or other support. Dargaville *et al.* (1996) found that ortho-linked oligomers of phenol were adsorbed more from an ethanol solution than the corresponding para-linked phenol oligomers. The difference was explainable by the greater ethanol-solubility of the para-linked compounds. Related findings are discussed in the next section.

#### *Solubility of the sorbate molecules in water*

Several studies have found correlations between adsorption capacity and decreasing water-solubility of the sorbate (Daifullah and Girgis 1998, 2003; Nouri *et al.* 2002b; Dąbrowski *et al.* 2005; Wu and Yu 2006a; Aktar *et al.* 2007a; Hamdaoui and Naffrechoux 2007a; Thuy *et al.* 2008; Navarro *et al.* 2009; Hansen 2010; Zhang *et al.* 2011c). An example is shown in Fig. 6, which is from the data of Thuy *et al.* (2008). As shown, there was a log-log relationship between the adsorption tendencies (Freundlich main coefficient) and the partition coefficient of the four pesticides between water and octanol.



**Fig. 6.** Log-log (base ten) relationship between the Freundlich “*K*” coefficient and the octanol-water partition coefficient for four pesticides adsorbing from water onto natural organic matter present in river water. Data replotted from the study of Thuy *et al.* (2008).

Similarly, Boving and Zhang (2004) showed that the rate at which aromatic hydrocarbons desorbed from aspen wood fibers was proportional to their water-solubility. Thus, the interaction between the sorbate molecules and water may often play a major role in determining the degree of success of adsorption as a procedure to remove a contaminant from water. Whightman and Fein (1999) identified the molecular characteristics governing the water-solubilities of chlorinated phenols. Findings of increased adsorption with decreasing water-solubility are sometimes explained in terms of a partitioning of the sorbate between the solubilized phase and an adsorbed state (Xia and Ball 1999).

Water-solubility does not always predict adsorption of petrochemical compounds in an expected way. For instance, a study by Yu *et al.* (2008) was notable with respect to its contrary finding that adsorption increased with increasing water-solubility of the three endocrine-disrupting compounds. Vismara *et al.* (2009) reported that a certain type of activated carbon, modified by polymer grafting, had high affinity for nitrophenols, which are somewhat hydrophilic compared to other phenols. The finding was attributed to the polarity of the polymeric chains grafted onto the adsorbents.

#### *Ionic charge of the adsorbate*

The majority of studies represented in Table A were concerned with sorbate species in their neutral state of charge. However, phenolic compounds are well known to acquire a negative charge if the pH is raised sufficiently. Thus the  $pK_a$  values (negative logarithms, base 10, of the acid dissociation constants) are generally in the pH range from about 6 to 10 (Daifullah and Girgis 1998). In addition, various studies have focused on sorbate species bearing strongly dissociated functional groups, such that an ionic charge was expressed over the whole studied range of pH (Yu *et al.* 2009; Yu and Hu 2011). Yu *et al.* (2009) proposed an ion exchange mechanism to account of the adsorption of perfluorooctane sulfonate and perfluorooctanoate, both of which will be present in dissociated form to give negatively charged surfactant species. Müller *et al.* (1980) noted that the adsorption of weak electrolytes (those that are not fully dissociated) can be predicted to a large degree by knowing the pH and the  $pK_a$  values. Li *et al.* (2012) reported cases in which increasing ionization of weak acid groups (the phenolic groups) resulted in less adsorption of chlorophenols. Such results are consistent with the solubility considerations discussed earlier.

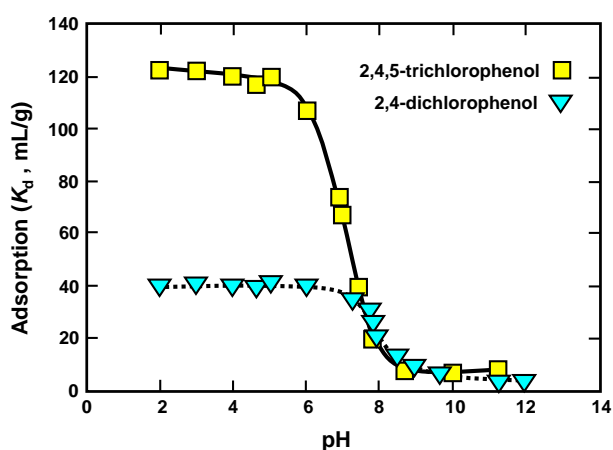
### **Effects of Aqueous Conditions**

Having considered the influences of adsorbent properties and adsorbate properties, it remains to consider the findings of studies that mainly have investigated the effects of differences in aqueous conditions.

#### *pH of the aqueous solution*

As listed in the “Key Findings” column of Table A, the pH of the aqueous medium was found to have a significant effect on adsorption in many of the surveyed studies. In particular, pH appeared to affect the adsorption of phenolic compounds onto cellulose-based materials, including activated carbons. In a majority of cases it was reported that adsorption fell when the pH was raised to about 10 or above, which is high enough to cause dissociation of phenolic hydrogens (Snoeyink *et al.* 1969; Moreno-Castilla *et al.* 1995b;

Severtson and Banerjee 1996; Kao *et al.* 2000; László and Szucs 2001; Rengaraj *et al.* 2002a; Lu and Chang 2005; Nouri and Haghseresht 2005; Ayranci and Duman 2006; Diaz-Flores *et al.* 2006; Srivastava *et al.* 2006; Wang 2007a; Blanco-Martínez *et al.* 2009; Nabais *et al.* 2009; Ofomaja and Unuabonah 2011; Rodrigues *et al.* 2011, 2013; Abdallah 2013). Figure 7, based on data from Severtson and Banerjee (1996), shows typical behavior. Some studies reported a maximum in adsorption at an intermediate pH (Rao and Viraraghavan 2002; Ahmaruzzaman and Sharma 2005; Ayranci and Duman 2006; Ncibi *et al.* 2006; Thawornchaisit and Pakulanon 2007; Memon *et al.* 2008; Bayramoglu *et al.* 2009; Li *et al.* 2009; Jamil *et al.* 2011; Rodrigues *et al.* 2011; Kumar *et al.* 2012; Ozdemir *et al.* 2012; Abdallah 2013; Kumar *et al.* 2014), though in most of these cases as well, the adsorption dropped off strongly with further increases in pH.



**Fig. 7.** Effect of pH on the adsorption of two chlorinated phenols onto softwood fibers having moderately high lignin content (Kappa number 69.8). Data replotted from Severtson and Banerjee (1996).

Other studies reported a general increase in adsorption of phenolic compounds with decreasing pH (Müller *et al.* 1985a,b; Shimizu *et al.* 1992; Jacobsen *et al.* 1996; Brandt *et al.* 1997; Namasivayam and Kavitha 2003; Nouri and Haghseresht 2004; Villacanas *et al.* 2006; Gao and Wang 2007; Kennedy *et al.* 2007; Nath *et al.* 2008; Correa 2009; Mathialagan and Viraraghavan 2009; Navarro *et al.* 2009). In yet other cases the best adsorption of phenolic compounds was observed at strongly acidic pH (Aksu and Yener 2001; Brás *et al.* 2005; Mohanty *et al.* 2005; Akhtar *et al.* 2006; Mestre *et al.* 2007; Ashour *et al.* 2008; Pigatto *et al.* 2013).

All such results, mentioned so far in this subsection, are consistent with increasing repulsion between the generally negative ionic charge of cellulose-based surfaces (due mainly to carboxylic acid groups) and the increasingly negative character of phenols as they are converted to their phenolate form at very high pH (Severtson and Banerjee 1996; Dąbrowski *et al.* 2005; Nabais *et al.* 2009). Also, as explained by various researchers (Westall *et al.* 1985; Wightman and Fein 1999; Moreno-Castilla 2004; Rodrigues *et al.* 2013), higher pH conditions that cause dissociation of phenolic groups cause such

compounds to become more soluble in water and therefore less prone to adsorb, regardless of the nature of the adsorbent.

In rare cases, increasing adsorption of petrochemical compounds with increasing pH has been reported (Mahvi *et al.* 2004). Nanseu-Njiki *et al.* (2010) found that the adsorption of paraquat on sawdust was highest at high pH. Qu *et al.* (2008) observed increasing adsorption of nitrobenzene onto bacterial surfaces with increasing pH. Navarro *et al.* (2008) reported maximal adsorption of phenol onto seaweed at pH=10. Notably, many of these reported findings involved non-rigid, swellable cellulose-based materials. Thus increasing adsorption of various sparingly soluble materials with increasing pH might be attributable to a tendency of the biomaterial to swell and become more accessible under such conditions.

Diverse effects of pH also have been reported relative to biosorption of certain pesticides. Ju *et al.* (1997) reported an optimum adsorption of lindane at lower pH onto bacterial biomass. Sathishkumar *et al.* (2008) reported maximum adsorption of carbaryl onto activated carbon at pH 11. Zheng *et al.* (2010) found that adsorption of two triazine pesticides on biochar was highest at low pH. However, later work by Zheng *et al.* (2013) reported increasing adsorption of the antibiotic sulfamethoxazole onto biochars with increasing pH.

#### *Ionic strength*

The effects of ion concentrations in solution also have been studied. Some researchers reported a slight increase in adsorption of sparingly soluble petrochemical compounds onto activated carbons with increasing salt concentration in solution (Moreno-Castilla 2004; Anirudhan *et al.* 2009). Other studies have shown a slight decrease in phenol adsorption with increasing KCl or NaCl (Halhouli *et al.* 1997; Karahoyun *et al.* 2011). Kilduff *et al.* (1998) reported similar trends in the case of trichloroethylene onto activated carbon that had been pre-loaded with humic substances. Khan *et al.* (2010) found that even large concentrations of salt did not interfere with adsorption of dichloromethane onto activated carbons. Likewise, Liu *et al.* (2009) found that removal of n-alkanes onto *Rhodococcus erythropolis* biomass was tolerant of salt conditions corresponding to seawater. Nanseu-Njiki *et al.* (2010) found somewhat lower adsorption of paraquat onto sawdust in the presence of NaCl. Mathialagan and Viraraghavan (2009) found no effect of salt concentration on the adsorption of pentachlorophenol from aqueous solution onto fungal biomass. To summarize, as noted already by Jacobsen *et al.* (1996), the effects of ionic strength tend to be minor when compared to those of pH, as described in the previous subsection.

In the case of adsorption of lindane onto bacterial biomass, Ju *et al.* (1997) found a strongly positive effect of increasing ionic strength. Newcombe and Drikas (1997) reported a similar trend for adsorption of natural organic matter onto activated carbon. Such findings are consistent with screening effects, allowing more charged material to adsorb in adjacent sites on a sorbent surface (Newcombe and Drikas 1997). According to a mechanism described by Westall *et al.* (1985), charged species such as phenolate ions would be expected to become increasingly compatible with a non-aqueous phase with increasing salt concentration; however, the mechanism has not been strongly supported by more recent work.

Divalent ions appear to promote adsorption of phenolics onto activated carbon in some cases (Coughlin *et al.* 1968). Surprisingly, Ni *et al.* (2011) reported that adsorption of certain aromatic carboxylate species was insensitive to either  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$ .

#### *Oxygen content of the aqueous solution*

A number of researchers have found that the adsorption of phenolic compounds onto cellulose-based sorbents, including activated carbons, can be affected by the concentration of oxygen in the solution (Nakhla *et al.* 1992; Abuzaid and Nakhla 1994; Uranowski *et al.* 1998). The explanation appears to be that the oxygen can favor an oligomerization reaction at the sorbent surface (Abuzaid and Nakhla 1994). In related work, Alvarez *et al.* (2009) showed that simultaneous ozonization and adsorption of gallic acid was a promising combined approach to remove it from solution.

#### *Temperature*

Effects of system temperature are shown in Table A in the column labeled “thermodynamics”. A great many studies have included an analysis of whether changes in the temperature of equilibration would either increase or decrease the adsorption capacity of cellulose-based materials for various petrochemical compounds. The label “En”, which stands for *endothermic*, means that heat was taken up when the adsorbate became attached to the surface of the adsorbent. The label “Ex”, for *exothermic*, means that heat was released during the adsorption event. As can be seen from the tabulated findings, both endothermic and exothermic behaviors have been widely reported. One complicating factor is that increased temperature can be expected to increase rates of adsorption, even in cases where there is minimal effect on the adsorption capacity (Chung *et al.* 2007). Thus, there is some possible difficulty in interpretation in cases where it is not clear whether or not equilibrium conditions of adsorption had been reached.

#### *Agitation*

Increased initial rates of uptake of petrochemical species onto adsorbents in the presence of agitation have been reported in a few cases (Koumanova *et al.* 2003; Chung *et al.* 2007; Jamil *et al.* 2011). Alam *et al.* (2007) found the best results for adsorption of 2,4-dichlorophenol onto activated carbon at an intermediate level of agitation. The fact that so few cases have shown significant effects due to agitation of adsorbent particles suspension suggests that factors other than diffusion to the surface of the adsorbent usually play a more prominent role in affecting adsorption.

#### *Presence of surfactants*

Gotovac *et al.* (2006) reported that the presence of surfactants affected the rate of adsorption of phenanthrene from ethanol solution onto carbon nanotubes. The sorbent material had been dispersed either with sodium dodecylsulfate or sodium dodecylbenzenesulfonate. The fact that the adsorption isotherms for the two systems were different from each other provides evidence for a strong interaction between the phenanthrene and the surfactant.

*Other solvent media*

Though the focus of this review article is on aqueous media, it can be revealing to consider results from a few studies involving adsorption of petrochemicals from other fluid media. Seredych and Bandosz (2010, 2011) studied adsorption of dibenzothiophene and 4,6-dimethyldibenzothiophene from simulated diesel fuel onto activated carbon. Results were found to be consistent with the pore size distribution and the size of the sorbate molecules. Zazharov *et al.* (2010) studied adsorption of phenol from mixtures of water and either dimethylsulfoxide or acetonitrile. Leva-Ramos *et al.* (1999) compared adsorption of phenol from aqueous and cyclohexane solutions. Greater adsorption was found in the case of the aqueous system. In general, one can expect greater solubility of various petrochemical compounds in non-aqueous media, and this difference may account for reduced adsorption in most of the reported cases.

*Competition for adsorption sites*

The topic of competitive adsorption between different petrochemical species will be considered at this point. In other words, one wants to know whether it makes a difference whether the aqueous system contains one adsorbate compound or two. Various articles have set out to answer that question. In many cases it has been reported that the adsorption of one species tended to inhibit the adsorption of another species (Fritz and Schlunder 1994; Srivastava and Tyagi 1995a; Ha and Vinitnantharat 2000; Haghsersht *et al.* 2003; Yang *et al.* 2006b; Ashour *et al.* 2008; Li *et al.* 2010a; Wei and Seo 2010; Kong *et al.* 2011b; Yu and Hu 2011; Mubarik *et al.* 2012; Sulaymon *et al.* 2013). Li *et al.* (2010b) found competitive effects between pyrene and phenol in the case of one type of activated carbon, but not in the case of a second type of activated carbon. Likewise, Cao *et al.* (2009) observed strong competition between atrazine and lead for adsorption onto activated carbon, but little competition in the case of biochar. Sometimes the competitive species are already present, due to the source of the adsorbent material (Cabrera *et al.* 2011). In particular, humic acids and other natural organic matter adsorbed onto biochar or activated carbon has been shown to compete for adsorption sites with various petrochemicals that may be present in soils or effluents (Kilduff *et al.* 1998; Newcombe *et al.* 2002b; Quinlivan *et al.* 2005; Karanfil *et al.* 2006; Yu *et al.* 2008; Ji *et al.* 2010; Li *et al.* 2010a; Yu and Hu 2011). In other cases minor or no competitive effects were observed (Bell and Tsezos 1998; Barbour *et al.* 2005; Cao *et al.* 2009; Chen *et al.* 2010). Certain of these “no significant competition” cases involved pairs of adsorbates having such different character (*e.g.* a metal ion and a petrochemical) such that one can easily expect interaction with different classes of surface site (Cao *et al.* 2009). However, in other cases very different types of sorbate were found to compete with each other for adsorption sites (Kong *et al.* 2011b). Chen *et al.* (2010) explained an instance of non-competition by proposing that adsorption was governed by partitioning between an aqueous phase and an oleophilic adsorbed phase having ample capacity.

Some investigators have noted that competition effects can be more pronounced near the beginning of an isotherm, *i.e.* when the bulk concentration of the adsorbate is very low (Yang *et al.* 2006b). Such behavior implies that a minority of sites may have higher affinity for the sorbate (Kilduff *et al.* 1998). As a logical extension, one might expect that competition would be more evident at relatively high levels of coverage if there is unequal



affinity for different adsorbates on the less-favorable sites (*i.e.* the last sites to be filled) on the adsorbent surface.

Liu and Pinto (1997) noted that, in a sense, all systems involving adsorption from solution should be considered in terms of competition, since the adsorbate species needs to compete with the solvent molecules, *i.e.* the water molecules, for adsorption sites. The importance of this effect was observed by Miyake (2003), who studied the adsorption of trichlorethylene from moist air onto activated carbons.

## THEORETICAL ASPECTS

The goal of this section is to review what has been published regarding how to explain various observed adsorption effects in terms of underlying mechanisms and models. Aspects to be considered can be grouped into the areas of molecular-level and colloidal forces, equilibrium aspects of adsorption (including isotherms), kinetic aspects of adsorption, and finally the modeling of semi-continuous “packed bed” systems for removal of petrochemicals from aqueous solutions using cellulose-derived adsorbents. The present discussion builds upon progress as described in previous review articles on the topic (Cookson 1978; Michalak *et al.* 2013).

### Van der Waals Interactions

The adsorption of hydrocarbons and aromatic compounds is very profoundly influenced by van der Waals forces. The London dispersion component of van der Waals forces results in attraction between all objects in the universe – including both atoms and larger objects (Liang *et al.* 2007). The range over which these forces are strong extends to about a wavelength of light, and as a consequence, such forces can be very important with respect to interactions between an adsorbate molecule and the adsorbent. Though the London dispersion component of force does not involve fixed electronic charges or polarity, it depends very strongly on the polarizability of electrons in the outer shells of the molecules under consideration (Visser 1972). Thus, somewhat higher London dispersion forces of attraction can be expected in the case of adsorbate molecules and adsorbents that have less strongly held electrons, such as those in the iodine or bromine atom or those associated with aromatic rings. The equations and constants governing such interactions have been well discussed and tabulated elsewhere (Visser 1972; Bowen and Jener 1995).

Because most of the studies considered in the present work involve adsorbates having moderate to strong hydrophobic character, and a majority of the studied compounds were uncharged under the conditions of testing, it is unsurprising that van der Waals forces have been very often proposed as being a key driving force for adsorption onto cellulose-derived substrates (Ju *et al.* 1997; Radobic *et al.* 1997; Franz *et al.* 2000; Jung *et al.* 2001; Haghsresht *et al.* 2002b; Juhasz *et al.* 2002; Nouri *et al.* 2002b; Villacanas *et al.* 2006). In the cited studies it was generally not possible to attribute adsorption to other likely classes of force, *e.g.* attraction between opposite charges or hydrogen bonding. One gets a sense that researchers sometimes have relied on a process of elimination in attributing adsorption to van der Waals attractions. Indeed, some of the strongest evidence demonstrating the importance of the London dispersion forces involves systems in which substantial adsorption was observed in spite of there being repulsion between negative

ionic charges on both the adsorbent and the adsorbate (Haghseresht *et al.* 2002b; Villacanas *et al.* 2006). Another form of evidence supporting a prominent role of dispersion forces is the influence of substituent groups on aromatic rings; by affecting the electron density and polarizability of the aromatic structures, the substituent groups of different electronegativity can be expected to change the strength of adsorption (Nouri *et al.* 2002b).

#### *Hydrophobic interactions*

The term “hydrophobic interactions” has been widely used to account for cases in which the hydrophobic parts of molecules in aqueous solution either self-associate or come out of solution to face towards a hydrophobic solid or air (Widom *et al.* 2003; Meyer *et al.* 2006). Thus the term has been used by some researchers to explain aspects of adsorption of petrochemical compounds onto cellulose-derived adsorbents (Ju *et al.* 1997; Rubin *et al.* 2006; Pan and Xing 2008; Yu *et al.* 2009; Pan *et al.* 2010; Hu *et al.* 2011; Plazinski and Plazinska 2011; Zhang *et al.* 2011a,b,c; Kong *et al.* 2012; Cong *et al.* 2013; Olivella *et al.* 2013; Zheng 2013). An important point to bear in mind is that in addition to the London dispersion forces acting between the hydrophobic entities, probably an even greater contribution to observed hydrophobic effects is due to hydrogen bonding and other polar interactions that occur within the aqueous phase. The free energy of the system as a whole is maximized when the hydrophobic groups either self-associate or become involved in adsorption, essentially getting out of the way of the groups capable of hydrogen bonding with each other (Moreno-Castilla 2004). Another important point to bear in mind is that cellulose itself can display substantial hydrophobic character, depending on circumstances, due to the self-integration of most of the hydrogen bondable sites (Medronho *et al.* 2012). Biochars and activated carbons, due to their greater aromatic nature and lower content of oxygenated groups, can be substantially hydrophobic in character (Ahmad *et al.* 2012; Ibrahim *et al.* 2013). As noted by Meyer *et al.* (2006) certain hydrophobic effects can be amplified and made to appear longer in range if the system contains tiny bubbles of air.

#### **Pi ( $\pi$ ) Bonding**

The terms  $\pi$ -bonding and  $\pi$ -stacking imply that organic compounds arrange themselves with the aromatic groups in a preferred orientation relative to each other. At present there does not appear to be a consensus regarding the origin of these forces, and some researchers have even questioned their existence (Grimme 2008). Three likely explanations for the appearance of strong affinity between aromatic structures include (a) the strength of London dispersion forces that may arise due to the delocalization and polarizability of electrons in aromatic rings, (b) polar interactions between electron-rich and electron-poor parts of molecules, and (c) the hydrophobic effect, as discussed in the previous subsection.

The action of  $\pi$ -bonding has been used to account for strong adsorption of certain aromatic species to activated carbons and other aromatic-rich plant-derived adsorbents (Jung *et al.* 2001; Haghserest *et al.* 2002b; Terzyk 2003a,b; Alvarez *et al.* 2005; Dąbrowski *et al.* 2005; Diaz-Flores *et al.* 2006; Wang *et al.* 2007a; Nabais *et al.* 2009; Rodrigues *et al.* 2011; Zhang *et al.* 2011b; Fu *et al.* 2012a; Zheng *et al.* 2013; Soni and Padmaja 2014). Other authors have noticed a similarly high affinity of aromatic compounds for aromatic-containing adsorbents but have explained the effect differently, stating that the relatively strong adsorption is due to the fact that flat hydrophobic faces of the “aromatic nuclei” are

able to interact strongly with adsorbate surfaces (Calace *et al.* 2002). Certain authors noticed that electron-withdrawing groups tended to decrease adsorption (Salame and Bandosz 2003; Moreno-Castilla 2004; Dąbrowski *et al.* 2005); this effect was attributed to a decreased electron density in the  $\pi$  system, thus decreasing the polarizability of the  $\pi$  electrons. Likewise, Diaz-Flores (2006) proposed that the presence of basic sites on the adsorbent made  $\pi$ - $\pi$  interactions stronger for the adsorption of pentachlorophenol onto activated carbons. Qu *et al.* (2008) observed strong adsorption between 1,3-dinitrobenzene and bacterial surfaces and proposed that an acid-base interaction is involved (see later) between deprotonated oxygen of carboxyl groups with the  $\pi$  electrons of 1,3-dinitrobenzene.

The most serious objection that has been raised relative to the face-to-face  $\pi$ -stacking model for adsorption of aromatic compounds to activated carbons (Sinnokrot *et al.* 2002) appears to be that of Haghseresht *et al.* (2002a). These authors proposed that the model aromatic compounds that they studied tended to adsorb by their edges, *i.e.* in a “T” arrangement. For electrostatic reasons the aromatic rings may stack themselves in an off-set arrangement, so that the electron-rich regions in the interior of aromatic rings can be adjacent to electron poor hydrogens on neighboring aromatic rings. Also, work has shown that effects very similar – and sometimes stronger – than interaction between adjacent aromatic compounds can be achieved by analogous molecular structures having very similar architecture, but lacking aromaticity (Bloom and Wheeler 2011). In summary, one needs to be quite skeptical of any claims that adsorption of aromatic compounds onto activated carbon or other adsorbents is conclusively attributable to  $\pi$ -bonding or  $\pi$ -stacking. More research is needed in order to resolve questions regarding use of the  $\pi$ -bonding concepts and their possible replacement with other approaches to interpret adsorption phenomena.

## Hydrogen Bonding

It is well known that hydrogen bonds can form in systems where hydrogen is covalently bonded to oxygen, or to a lesser extent to other relatively electronegative atoms such as nitrogen (Jeffrey 1997; Maréchal 2007). Because of the unfair sharing of electrons between the hydrogen and its electronegative partner, the hydrogen takes on part of the character of a bare proton. This unusual circumstance gives rise to hydrogen bond formation between such protons and the lone pairs of electrons on neighboring oxygens in the system. Considering the bonds within cellulose as an example, a typical hydrogen bond has an energy of about 19 kJ/mole (about 4 to 5% the energy of a covalent bond between O and H), a distance that can be 2 to 2.5 times the length of a corresponding covalent bond between O and H (Li *et al.* 2011), and an average lifetime of only about 250 picoseconds under ordinary ambient conditions (Belashchenko *et al.* 2014).

As was briefly suggested in an earlier paragraph dealing with hydrophobic bonding, the most important contributions of hydrogen bonding to the adsorption of substantially oxygen-free compounds onto cellulose-derived substrates may be indirect. That is, the extensive hydrogen bonding within the aqueous phase provides a thermodynamic driving force encouraging the exclusion of molecules or molecular segments that lack hydrogen bonding ability. The high cohesive energy within an aqueous phase (2.30 kJ/cm<sup>3</sup>) is considerably larger than that of a typical organic solvent such as heptane (0.23 kJ/cm<sup>3</sup>) or

even benzene ( $0.35 \text{ kJ/cm}^3$ ) (Kolker *et al.* 2005). A sharp contrast between the cohesive forces acting in an aqueous phase and those acting within typical organic solvents is shown in the following table of the Hansen solubility parameters (Hansen 2007).

**Table 1.** Hansen Solubility Parameters for Three Pure Liquids

Liquid type	Dispersion forces	Polarity	Hydrogen bonding
Water	15.5	16.0	42.3
Hexane	14.9	0.0	0.0
Benzene	18.4	0.0	2.0

As shown in Table 1, the non-polar liquids have almost no ability to participate in hydrogen bonding. It follows that the presence of hydrophobic compounds in the aqueous phase is unfavorable in terms of enthalpy, *i.e.* with respect to the forces of interaction. Random diffusion (*i.e.* entropy effects) largely accounts for the moderate aqueous solubility of phenols, hydrocarbons, and many other such compounds. Phase separation occurs spontaneously above a certain concentration (Hansen 2007). But the same thermodynamic tendencies leading to phase separation often can promote adsorption of the compounds in question onto suitably hydrophobic substrates.

Another aspect of hydrogen bonding that may potentially have a big effect on the adsorption of petrochemical compounds onto cellulose-derived adsorbents is the local structure of water (Farrell *et al.* 1999; Joo *et al.* 2008). Many studies have shown that the presence of a surface or another compound may either increase or decrease the degree of organization, *i.e.* the ice-like character of the closest layers of water (Park *et al.* 2007). As noted by Meyers *et al.* (2006), many researchers have invoked water structure as a contributing factor leading to the self-agglomeration and/or adsorption of hydrophobic compounds originally present in aqueous solution. The idea is that the presence of a non-hydrogen bonding entity causes the adjacent water to become more organized, thus decreasing the entropy of the system. Exclusion of the non-hydrogen-bonding entities from the solution by their adsorption to a surface increases the system's randomness, thus providing a thermodynamic driving force in favor of adsorption, depending on the details of the situation.

Most researchers studying the role of hydrogen bonding in adsorption of petrochemicals from aqueous solution onto cellulose-related adsorbents have focused on hydrogen bonding between the adsorbate and the adsorbents. Several authors reported evidence that hydrogen bonding makes a positive contribution to such adsorption (Franz *et al.* 2000; Nevskaia and Guerrero-Ruiz 2001; Blackburn *et al.* 2007; Chen and Li 2007; Navarro *et al.* 2008; Plazinski and Plazinska 2011; Fu *et al.* 2012a). Nevskaia and Guerrero-Ruiz (2001) based their attribution regarding hydrogen bonding to the relatively easy thermal desorption of nonylphenol. Franz *et al.* (2000) cited the thesis work of Leng (1996), who compared the adsorption of phenol from water and from cyclohexane onto oxygenated carbon; increased adsorption from the organic solvent, which cannot form hydrogen bonds, was taken as evidence that the phenolic group was interacting with the surface-bound oxygens. Franz *et al.* (2000) carried out a similar analysis for a wider variety of adsorbates and reported similar findings. Navarro *et al.* (2008) argued that strong hydrogen bonding is promoted by the presence of an ionized phenolate group, which can

interact with available –OH groups on the adsorbate. The concept was attributed to earlier workers, such as Iqbal *et al.* (2005). Blackburn *et al.* (2007) backed up their conclusions with computational chemistry results, which showed the feasibility of Yoshida-type hydrogen bonding between a phenolic –OH group and the –OH groups of cellulose. Plazinski and Plazinska (2011) supported their statement by molecular dynamics simulations. By contrast, Zhang *et al.* (2011a) ruled out hydrogen bonding as being a significant contribution to adsorption of simazine to biochars based on an analysis of Freundlich affinity coefficients (see later). Zheng *et al.* (2013) used the concept of charge-assisted hydrogen bonding to explain an observation of increased sorption of the antibiotic sulfamethoxazole onto certain biochars. In summary, while researchers have reported a role of hydrogen bonding in the adsorption of petrochemicals, especially in the case of adsorption of phenolic compounds, there is no consensus that such contributions have major importance.

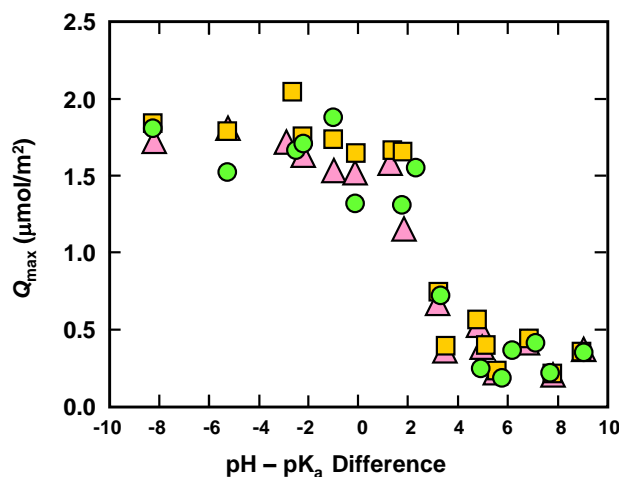
### Electrostatic Interactions

The topic of electrostatic interactions involves several aspects, including not only the attractions and repulsion between ions, but also various acid-base effects that do not involve ionization, as well as issues related to polar compounds. Since the focus of this article is on adsorption from aqueous media, it makes sense to consider the ionic interactions first.

Ionic interactions have been proposed as having a major influence by many researchers who have studied adsorption of petrochemicals onto cellulosic materials and activated carbons (Radobic *et al.* 1997; Nouri *et al.* 2002a,b; Ayranci and Dyman 2006; Villacanas *et al.* 2006; Blackburn *et al.* 2007; Zhang *et al.* 2011c; Fu *et al.* 2012a). Some of the strongest evidence supporting a major role of ionic attractions and repulsions in the adsorption of petrochemical compounds to cellulose-derived substrates comes from studies of pH effects, as covered in an earlier section (see, for instance, Brandt *et al.* 1997; Ayranci and Dyman 2006). Also, ionic species can take part in ion-exchange, as a contributing factor in their adsorption (Wu *et al.* 2003; Yu *et al.* 2009). Figure 8 represents data from Haghseresht *et al.* (2002), who studied adsorption of benzoic acid, *p*-cresol, *p*-nitrophenol, and salicylic acid onto three commercial activated carbons. As shown, they found that the results were closely related to the difference between the pH value and the  $pK_a$  value. When this difference is negative (at the left side of the plot), the phenolic and other weakly acidic compounds were mainly in their uncharged state, and adsorption was strong, despite the negative charge associated with typical activated carbon surfaces at intermediate to alkaline pH conditions. By contrast, adsorption was strongly reduced under conditions at the right-hand side of the plot, where one would expect both the adsorbate compounds and the adsorbent surface each to bear a negative ionic charge.

A majority of the cited systems that were found to be strongly pH-dependent were those involving phenolic adsorbents; the  $pK_a$  values of various phenols depend on the electronegativity of substituents on the phenol's aromatic ring. The  $pK_a$  value of phenol itself is about 10 (Daifullah and Girgis 1998). But the  $pK_a$  value can range from 5.4 (for 2,4-dinitrophenol), to 10.3 (for *p*-cresol). A low value of  $pK_a=4.7$  has been reported in the case of pentochlorophenol (Crosby 1981), which is consistent with very strong withdrawal of electron density from the ring, thus stabilizing the anionic phenolate species. Moreno-Castilla *et al.* (1995b) found a rough agreement between such  $pK_a$  values and the influence

of pH on the adsorption of two phenols. However, there is a critical need for research that compares a series of different phenols onto a specified adsorbent over a range of pH values. In principle, adsorption would be expected to fall off under conditions in which the phenols in question spend a high fraction of their time in a negatively charged ionic state, giving rise to electrostatic repulsion with anionic carboxylate groups present on typical cellulose-derived adsorbents, including activated carbon products.



**Fig. 8.** Dependency of adsorption capacity on the difference between pH and the pK<sub>a</sub> value of selected weakly acidic compounds having a single aromatic ring. The three symbols correspond to three different commercial activated carbons.

### Acid-Base Interactions

Even in cases where surfaces are not ionized, there still can be important electrostatic contributions to molecular interaction due to Lewis acidity and basicity. The subject of Lewis acids and bases, including explanations of how this type of interaction differs from Brønsted acidity and basicity, has been well described elsewhere (House 2013). While ionic species, *i.e.* Brønsted acids and bases, are often dominant in aqueous systems, Lewis acidity and basicity can express themselves in non-aqueous environments. The petrochemicals considered in this review article include many quite hydrophobic compounds, and typical activated carbon products are hydrophobic too. It is reasonable to expect, in such cases, that the adsorbing hydrophobic species might force water molecules away from the interface with the adsorbent, creating a local non-aqueous environment.

As noted in review papers by Shen (2009) and Gamelas (2013), lignocellulosic materials typically contain both acidic and basic Lewis sites at their surfaces. Ahmad *et al.* (2013) noted that the surfaces of activated carbons tend to be dominated by acidic groups after preparation at relatively low temperatures, whereas basic Lewis sites often predominate in carbons pyrolyzed at relatively high temperatures. Strong correlations have been found between Lewis basicity and the content of  $\text{C=O}$  groups, which are able to contribute electron density (Shen *et al.* 1998). Furthermore, the Lewis acidic or basic surface character of activated carbon can be affected by post-treatment (Dąbrowski *et al.* 2005).

Several groups of researchers have proposed that acidic or basic sites play a role in the adsorption of various petrochemical compounds either on lignocellulosic materials or

on their pyrolyzed forms (Tessmer *et al.* 1997; Daifullah and Girgis 2003; Terzyk 2003b; Diaz-Flores *et al.* 2006; Hu *et al.* 2011; Fu *et al.* 2012a; Ahmad *et al.* 2013). According to Dąbrowski *et al.* (2005), the greater the ratio of acid to basic groups, the lower will be the adsorption of phenol. Franz *et al.* (2009) concluded that donor-acceptor interactions were not significant in their study of adsorption of various aromatic compounds onto activated carbon. In fact, in none of the studies just cited was there undisputable evidence that it was the Lewis form of acidity or basicity, rather than consequent ionization of the surface, that affected adsorption.

### Solubility Concepts Relative to Adsorption

Another way to attempt to account for different types of contribution to adsorption phenomena is by considering the mutual solubility of the adsorbate in the adsorbent material. Such an approach has become widely applied in order to predict whether a given polymer will dissolve in a given solvent system (Hildebrand 1936; Hansen 2007; Rosenholm 2010). The concept also has been used to predict wetting and adhesion phenomena (Good 1992). To apply a solubility approach to predicting whether or not a given adsorbent will have strong affinity for a given adsorbate surface, one compares certain aspects of each of them, such as the Hildebrand parameter (defined as the square-root of the cohesive energy density) and the tendency of both the adsorbate and adsorbent to form hydrogen bonds. A mis-match regarding either of these factors implies less compatibility. Browne and Cohen (1990) showed that the Hildebrand solubility parameter could be used to compare the solubilities of different sorbates, therefore helping to explain the relative tendencies of chloroform and trichloroethylene to adsorb onto activated carbon.

One situation in which a solubility approach appears to be especially appropriate is when the substrate contains a portion of solvent-like compounds such as waxes or residual oils (Lin *et al.* 2007; Li and Chen 2009). Also, solubility considerations such as the partitioning of adsorbate between two phases have been applied when the adsorbate is a soft, swellable material, such as fruit cuticles (Li and Chen 2009) or never-dried fungal biomass (Chen *et al.* 2010, 2011). In some cases the adsorbate may actually become bound to solubilized polymers that are released from a substrate (Choi *et al.* 2003). Alternatively, it was found that derivatizing the surface of sawdust with fatty acid chains was beneficial for the removal of oleic acid and olive oil from water (Maurin *et al.* 1999); the cited study provides a clear example of how chemical similarity between the adsorbent's surface and the adsorbate can promote sorption.

Abe *et al.* (1985) carried out a unique analysis in which they considered the contributions of individual types of atoms toward adsorption of pollutants onto activated carbon. Carbon, bromine, and chlorine atoms on the adsorbent surfaces were found to have a positive effect on adsorption, whereas oxygen atoms negatively affected adsorption, and hydrogen atoms had little influence. As noted earlier, Seredych and Bandosz (2011) found evidence that sulfur atoms on both the adsorbent and adsorbate can promote adsorption.

### Free Energy Change on Adsorption

In principle, by summing all of the interactive force contributions, it should be possible to predict the free energy of adsorption. Polanyi proposed that such an energy term could be used to predict adsorption outcomes (Manes and Hofer 1969). The cited authors used this approach and concluded that findings from gas-phase adsorption can be

used to predict adsorption from various solvents. Various other researchers have employed aspects of the Polanyi adsorption theory to understand adsorption of petrochemicals onto cellulose-derived adsorbents (Greenbank and Manes 1981; Aytekin 1991). Xia and Ball (1999) found close agreement between their data for adsorption of nine nonpolar compounds onto loam soil; they concluded from such evidence that adsorption involved filling of micropores, which was one of the theoretical predictions (see later). Yang *et al.* (2006a) likewise found good agreement with the Polanyi theory when studying adsorption of polycyclic aromatic hydrocarbons on various carbon-based adsorbents. Though not much research of this type has been reported, the approach appears well suited for confirmation by molecular dynamics simulation studies (Terzyk *et al.* 2010; Plazinski and Plazinska 2011). Advances in computing power and simulation programs offer the possibility in future studies of achieving greater quantification of interactive forces, while also taking into account the many possible conformations of adsorbed molecules.

### Adsorption Isotherms

The term “adsorption isotherm” refers to the portrayal of adsorption data obtained under quasi-equilibrium conditions. Either equations or their graphical representation are used in an isotherm to describe the relationship between the amount adsorbed and the concentration in an adjacent bulk solution. As the subject of adsorption isotherms was covered earlier in great detail (Hubbe *et al.* 2011), the main focus here will be on just the adsorption of petrochemicals onto cellulose-derived adsorbents. Readers who are particularly interested in the mathematical forms of various isotherms may refer to the earlier document. An attempt also will be made in this section to draw connections between the fitting of data to certain types of isotherms *vs.* what is likely to be happening at the molecular and nano-scale levels.

#### Langmuir isotherm

As can be seen from the fifth column of Table A (see Appendix), the Langmuir isotherm (Langmuir 1918) has been successfully used by many research groups to represent equilibrium amounts of various petrochemical compounds on various cellulose-related substrates. As was noted earlier (Hubbe *et al.* 2011), the Langmuir equations can be expressed in nonlinear and linearized forms as follows,

$$q_e = \frac{Q^o b C_e}{1 + b C_e} \quad (1)$$

$$C_e / q_e = 1 / Q^o b + C_e / Q^o \quad (2)$$

where  $q_e$  (mg/g) is the amount of adsorbed compound, and  $C_e$  (mg/L) is the corresponding concentration in the solution at equilibrium. The quantity  $b$  (L/mg) is a measure of the affinity of binding sites for the adsorbate, and  $Q^o$  (mg/g) is the adsorption capacity, based on a model in which each adsorbate molecule can fill one site and where there are no interactions between molecules adsorbing at adjacent sites.

From several perspectives it can be argued that the Langmuir model provides a superior approach for judging the suitability and performance of different adsorbents for



removing pollutants from aqueous (or other) solution. A good fit of data to the model yields a single value for the adsorption capacity  $Q^0$ , *i.e.* how much could the adsorbent material hold when all of the possible sites are filled. This is critically important information when one is judging which of two or more adsorbents would be able to effectively hold onto more of a given pollutant, especially in cases where there is a large amount of material that needs to be removed from the water. On the other hand, the value of  $b$  can be a convenient and concise way to judge which of several adsorbents would be likely to perform best in reducing the bulk concentration of a pollutant to a very low level. In addition to these two valuable pieces of information, it can be argued that the mere fact that there is a good fit with the Langmuir model provides evidence that an adsorbent system is well-behaved, providing a predictable capacity and a predictable affinity. In Table A much of the information in the column headed by “Adsorption capac. (mg/g)” comes from fits to the Langmuir model (as indicated by the letter “L” in the column headed “Isotherm best fits”). In cases where the authors did not report fitting results based on the Langmuir equation, the capacity values shown in the table are estimates based on an inspection of the reported data; in the course of making such estimates it was evident that such systems were often not as “well behaved” in terms of exhibiting a clear adsorption capacity.

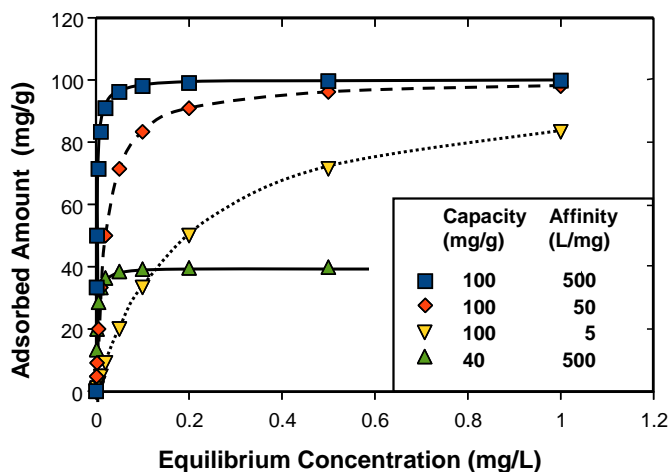
Table 2 provides some examples, taken from the surveyed literature, representing the wide ranges in terms of both capacity and affinity, based on Langmuir model fits. As can be readily seen, the two parameters are quite independent. For instance, a system reported by Blanco-Martínez *et al.* (2009) showed a combination of high adsorption capacity but low affinity. A system reported by Demirak *et al.* (2011) showed relatively low capacity but high affinity. A study of adsorption of the pesticide cypermethrin on cork showed an especially unpromising combination of low capacity and low affinity (Domingues *et al.* 2007). And a study by Daifullah and Girgis (1998) showed one of the most promising cases in the published literature, high capacity and very high affinity of phenols onto a certain activated carbon product.

**Table 2.** Selected Data Representing a Range of Langmuir Fit Coefficients

Adsorbent	Adsorbate	$Q^0$ (mg/g)	$b$ (L/ $\mu$ g)	Citation
DDD, DDE	Bagasse fly ash	0.007	37	Gupta & Ali 2001
Benzene, <i>etc.</i>	Angico sawdust	0.002-0.011	1-3	Costa <i>et al.</i> 2012
Ci-cypermethrin	Cork	0.1-0.3	0.1	Domingues <i>et al.</i> 2007
Dichlorophenol	<i>Posidonia ocean.</i>	1	660	Demirak <i>et al.</i> 2011
Dichlorophenol	Anaerobic sludge	1-7	6-64	Gao <i>et al.</i> 2007
Three pesticides	Date stones	6	1-2	El Bakouri <i>et al.</i> 2009
Phenols	Fungal biomass	42-289	10-40	Bayramoglu 2009
Phenol	Activated carbon	74-238	24-130	Fierro <i>et al.</i> 2008
Catechol	Activated carbon	178-238	4-6	Blanco-M. <i>et al.</i> 2009
Phenols	Activated carbon	232-339	200-600	Daifullah & Girgis 1998

Figure 9 illustrates how different values for the two parameters  $Q^0$  and  $b$  can result in quite different graphical output. As shown, a relatively high value of the affinity coefficient  $b$  implies that very little of the adsorbed species will remain in the dissolved phase at equilibrium, until the adsorbent material is almost fully saturated. By contrast, a relatively low value of  $b$  implies that more of the target compound is expected to remain

in solution, even though a high proportion of unoccupied sites may be available on the surfaces. As illustrated by the dash-dot curve, if one's main goal is to reduce the bulk concentration to near zero, there may be cases where the value of  $b$  is more important than the maximum amount of uptake, *i.e.*  $Q^0$ .



**Fig. 9.** Calculated values of adsorbed amounts based on the Langmuir model, using selected values of adsorption capacity  $Q^0$  and adsorption affinity  $b$

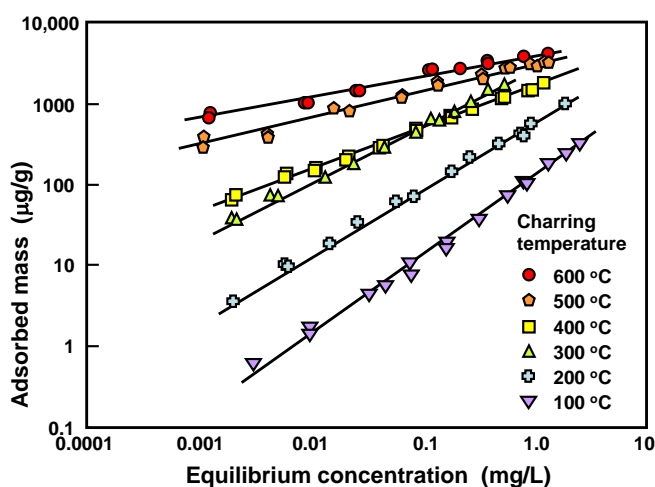
Many sets of adsorption data fail to achieve good fits to the basic form of the Langmuir model. Before abandoning such a promising model in such cases, one of the most practical alternatives to consider is the possibility that the surface has two or more distinct populations of adsorption sites, each of which is consistent with the Langmuir model. Thus, in a particular auspicious case, most of the sites might have moderately high affinity, but there might be a few sites with ultra-high affinity for the adsorbate. Such an adsorbent would have unique capability of being able to “scour” very highly dilute solutions and remove the last vestiges of a pollutant, while also being useful for high levels of removal when used to remove pollutant from more highly contaminated water. For example, Müller *et al.* (1980) proposed that electrostatic effects could shift local environments at an adsorbate surface, resulting in “patches” that can be represented by different Langmuir parameters. Related approaches have been used when accounting for the adsorption of multiple adsorbates from a mixture (Haghseresht *et al.* 2002c; Agarwal *et al.* 2013).

#### *Adsorption to heterogeneous sites*

Several groups of researchers have placed emphasis on the heterogeneity of adsorption sites in the systems that they studied (Snoeyink *et al.* 1969; Müller *et al.* 1980; Juang *et al.* 1996a; Kilduf *et al.* 1998; Franz *et al.* 2000; Hsieh and Teng 2000; Nouri *et al.* 2002a; László *et al.* 2003, 2006; Podkościelny *et al.* 2003; Dąbrowski *et al.* 2005; Abdallah 2013). The empirical Freundlich (1907) isotherm equation is often used as a practical way to summarize adsorption data from such systems. Hsieh and Teng (2000) noted that in the systems they studied the adsorption of phenol was not proportional to the

determined surface areas of different activated carbons, and they therefore concluded from this observation that the adsorption sites must be heterogeneous. Dąbrowski *et al.* (2005) argued that both chemical and geometrical factors can account for differences in affinity of an adsorbate for different locations on an adsorbent. Rossner *et al.* (2009) proposed that some cases in which adsorbents exhibit heterogeneity in adsorption affinity are due to a distribution of pore sizes, with higher affinity associated with the smaller pores. It seems likely that locations within very fine pores can be favored because the tight concave curvature of the solid allows more of the solid surface to be exposed to an individual molecule of adsorbate (Farrell *et al.* 1999).

Figure 10 provides an example where fits to the Freundlich equation appear to show an important shift in the nature of adsorption phenomena as the temperature of biochar formation is increased (Zhang *et al.* 2011a). Note that increasing charring temperature changed not only the overall levels of adsorption, but also the slopes of the best-fit lines were changed. Such a shift is consistent with the enrichment of aromatic and hydrophobic surface groups, which offer strong affinity to the simazine pesticide even at very low levels of adsorbed amounts. By contrast, higher slopes were found for samples that had been subjected to lower temperatures of treatment. Such results are consistent with a lower affinity between the pesticide and the surface-bound groups at the lower level of charring. Thus, in those cases there would be a greater importance of self-association of the pesticide molecules with each other as a contributing factor leading to their adsorption.



**Fig. 10.** Freundlich plot of adsorbed amounts of simazine pesticide on biochars prepared from corn straw at various oxygen-limited temperatures. Data replotted from Zhang *et al.* (2011a)

#### Other isotherm models

A wide range of other equations, some empirical and some based on theoretical models, have been used to account for data that do not fit well to the Langmuir model. Some examples are cited in Table 3, which also lists some of the purported advantages or implications of such models. The arrangement of the rows places models that are most similar to the Langmuir model near to the top. Towards the bottom of the table one finds models used to fit data in cases where adsorption did not seem to be related to a definable population of surface sites.

**Table 3.** Selected Examples Where Isotherms Models Other than Langmuir Were Used to Account for Adsorption of Petrochemicals onto Cellulose-derived Adsorbents

Model and its Attributes	Citation
<b>Redlich-Peterson.</b> A heterogeneity factor is used together with an approach that is otherwise similar to the Langmuir model. The results converge to the Langmuir equation as the factor approaches unity. The equation is basically a combination of the Langmuir and the Freundlich equations.	Redlich & Peterson 1959; Aksu and Yener 2001; Ahmaruzzaman & Sharma 2005
<b>Temkin isotherm.</b> The heat of adsorption is assumed to decrease linearly with filling of adsorption sites. This implies that there is mutual repulsion between adsorbed molecules and similar dissolved molecules approaching adjacent adsorption sites.	Temkin 1941; Hamdaoui & Naffrechoux 2007a,b; Ahmad <i>et al.</i> 2013
<b>Dubinin-Astakhnov.</b> The cited authors show that this equation has advantages over the ordinary Langmuir equation to account for adsorption of phenols on activated carbons.	Stoeckli <i>et al.</i> 2001
<b>Fowler-Guggenheim.</b> The heat of adsorption is assumed to be varying in a linear manner with increasing adsorption. The model is consistent with lateral interaction between adsorbate molecules, which can be either attractive or repulsive.	Fowler & Guggenheim 1939; Hamdaoui & Naffrechoux 2007a
<b>Hill-de Boer.</b> Adsorbate molecules are assumed to be able to move, and the adsorption sites are assumed to have a range of adsorption energies. Lateral interaction among the adsorbed molecules can be positive or negative.	Hill 1946; de Boer 1953; Hamdaoui & Naffrechoux 2007a
<b>Kiselev.</b> Adsorption is assumed to take place as localized monomolecular layers.	Kiselev 1958.
<b>Dubinin-Radushkevich.</b> The model assumes that adsorption is dominated by the filling of pores, with a strongly increasing energy of adsorption with decreasing width of slit-like pores.	Dubinin 1975, 1989; Cal <i>et al.</i> 1994; Ahmad <i>et al.</i> 2013
<b>Elovich.</b> The sites that are available for adsorption are assumed to increase exponentially during the process of adsorption. The model is consistent with multi-layer adsorption.	Aharoni & Tompkins 1970; Tseng & Juang 2003; Hamdaoui & Naffrechoux 2007a
<b>Brunauer, Emmet, and Teller.</b> This model is widely used for determination of surface areas of solids by adsorption of very cold nitrogen or argon gases, under the assumption of a detectable transition from monolayer to multi-layer adsorption.	Brunauer <i>et al.</i> 1938; Rao & Viraraghavan 2002

#### *Low affinity adsorption*

The scientific literature in general has been shown to reflect a bias in favor of the reporting of successful results (Fanelli 2012). Thus, even when authors report especially low adsorption capacities and feeble affinity, words such as “successfully adsorbed” often appear in the concluding statements. Given this state of affairs, the discerning reader needs to adopt a strategic approach, looking for clues that might reveal inherent problems with certain combinations of adsorbate and adsorbent. Some such clues, which were noted during the current search of the literature, are summarized in Table 4.

**Table 4.** Clues to Identify Less-than-Promising Reported Adsorption Results

Evidence	Problematic Aspects	Examples Cited
Log-log plotting of data	A relatively high solution concentration may be required to achieve effective adsorption.	Brown & Cohen 1990; Sun <i>et al.</i> 2011b
Different models used for low & high ends of isotherm	The implications of the different models may be mutually incompatible.	Dąbrowski <i>et al.</i> 2005
Sorption increasing out of proportion with concentration	This may be a clue that the self-affinity of the adsorbate drives the process; it follows that the affinity between the adsorbate and adsorbent may be low.	Estevinho <i>et al.</i> 2006
Low value of accessible surface area	Even if the chemical composition favors sorption, the capacity may be low.	Olivella <i>et al.</i> 2013
Poor fit to Langmuir adsorption model	Such lack of fit can be a clue to low affinity behavior.	Chen <i>et al.</i> 2005
Natural, unmodified plant material, possibly dried	Some of the lowest reported capacities were with unmodified biomass.	Estevinho <i>et al.</i> 2006

#### *Bilayer adsorption*

Some experimental situations are best understood by assuming that target substances in the bulk of solution have a strong affinity for similar molecules that are already adsorbed. In the simplest case, the further progress of adsorption results in the gradual formation of a bilayer. Such behavior has been reported in the case of the antimicrobial agent chlorhexidine on cotton (Blackburn *et al.* 2007). Bilayer adsorption is especially found in the adsorption of cationic surfactants onto negatively charged, hydrophilic surfaces (Speranza *et al.* 2013). In such systems the cationic headgroups of the first layer face inwards to the negatively charged adsorbent surface, taking advantage of attraction of opposite charges. The second layer involves a favorable tail-to-tail interaction between the hydrophobic parts of the molecules. A third layer of cationic surfactant is not expected in such cases due to the fact that the adsorbed bilayer presents a hydrophilic, cationic layer towards the bulk of solution, and such a surface is unfavorable for adsorption of additional cationic surfactant molecules.

#### *Multilayer adsorption.*

Noting that cationic surfactants may be considered as a special case, it has been much more commonly reported that certain petrochemicals tend to form multilayers on various adsorbents, especially when their bulk concentration is relatively high (Bina *et al.* 2012) or when adsorption takes place from a gas phase (Bartholdy *et al.* 2013). The Brunauer-Emmett-Teller (BET) equation, which is often used for the analysis of surface areas of solid materials by adsorption of nitrogen or argon gas (*e.g.* Chen *et al.* 2012b; Isahak *et al.* 2013), has been shown to achieve a good fit to certain data from adsorption of petrochemicals onto cellulose-derived substrates from aqueous solution (Edgehill and Lu 1998; Rao and Viraraghavan 2002; Bina *et al.* 2012). In some other cases the BET isotherm was tried, but it was found not to fit certain data as well as more commonly used isotherm models, such as the Freundlich isotherm (Khan *et al.* 1997a). In the cited work of Bina *et al.* (2012) it is notable that evidence of multilayer adsorption was found for the adsorbate ethylbenzene, a relatively small molecule, for which hydrophobicity and low solubility (see

earlier) provide a driving force that favors self-association of the adsorbate in the adsorbed state.

#### *Pore filling models and hysteresis*

It does not require too much extension beyond a concept of multilayer adsorption before one passes into a somewhat different approach to predicting adsorption capacities – models in which the adsorption capacity is mainly determined by the void volume within a microporous or mesoporous adsorbent. Such a model has been proposed by many authors to account for the adsorption of various petrochemical compounds onto and into activated carbon products (Xia and Ball 1999; Ahmad *et al.* 2013; Hao *et al.* 2013; Ran *et al.* 2013). Chiu *et al.* (2003) found that a pore-filling model could account for toluene adsorption from the vapor phase onto peat, with the results not too far from the pore volume determined by nitrogen adsorption isotherms. Xia *et al.* (1999) observed the same limiting sorption capacity for a wide range of nonpolar organic chemicals, and they used this finding as evidence that void volume, rather than surface interactions, mainly provides the upper limit of sorption capacity in the studied systems.

It seems remarkable that few researchers dealing with adsorption of petrochemicals from aqueous solution have considered use of the Kelvin equation to account for adsorption phenomena (Hseih and Teng 2000). It is well known that the Kelvin equation predicts a decreased vapor pressure of liquid contained within a finely porous solid, depending on the contact angles (Adamson and Gast 1997; Beverley *et al.* 1999). As shown by the form of the Kelvin equation given below, the vapor pressure of adsorbate in a gas phase in equilibrium with a small pore can be strongly depressed, depending on the shape of the meniscus within the pore. The Kelvin equation can be written in the following form (Chen *et al.* 2006),

$$RT \ln(p/p_s) = V(p - p_s + 2\gamma \cos\theta/r) \quad (3)$$

where  $R$  is the gas constant ( $8314 \text{ J kmol}^{-1}\text{K}^{-1}$ ),  $T$  is the absolute temperature,  $p$  is the equilibrium vapor pressure,  $p_s$  is the same in the case of a flat interface,  $V$  is the volume of a mole of the liquid,  $\gamma$  is the interfacial tension,  $\theta$  is the contact angle with respect to the liquid in the capillary, and  $r$  is the radius of a capillary (modeled as a cylinder). Assuming perfect wetting of the internal liquid, the  $\cos\theta$  term approaches unity. While it is widely used to account for the condensation of gases in finely porous solids, the Kelvin model has been considered much less often for adsorption of dissolved compounds from aqueous solution onto micro- and mesoporous solids (Gun'ko *et al.* 2003; Chen *et al.* 2006). There does not appear to be any strong theoretical reason to doubt that the same principles hold true when a liquid within a capillary is adjacent to an immiscible liquid phase. In either case, the pressure difference due to the capillary forces will result in a difference in chemical potential on the two sides of the interface. In principle, depending on the contact angles at the adsorbate-aqueous-adsorbent interface at the entrance to an unfilled pore structure, one can expect that there to be bias in favor of adsorption, compared to adsorption onto outer surfaces of the adsorbent. This appears to be a neglected field in terms of both theory and practical demonstrations.

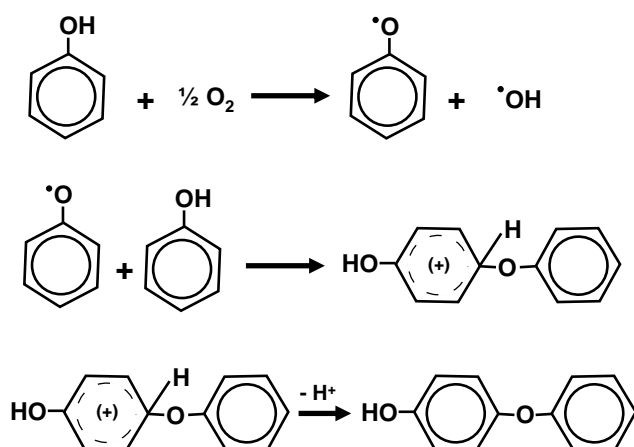
One type of evidence that can support the pore-filling concept involves hysteresis. In other words, the relationship between adsorbed amount and bulk concentration is

different, depending on whether the bulk concentration is being raised or lowered. Strong hysteresis could be expected based on a pore-filling model if the affinity between an adsorbate molecule and an adsorbent is strongly enhanced by the presence of condensed adsorbate molecules already occupying some of the pores. The Kelvin equation, as just introduced, predicts strong hysteresis in some cases, since a strongly curved meniscus can contribute to a strong suppression of desorption, beyond what would be expected for adsorption on a flat surface. Such a mechanism has been proposed by Farrell *et al.* (1999). Evidence of irreversibility of adsorption has been reported in many relevant cases (Snoeyink *et al.* 1969; Ferro-Garcia *et al.* 1996; Pignatello and Xing 1996; Farrell *et al.* 1999; Ning *et al.* 1999; Ha and Vinitnantharat 2000; Pan and Xiing 2008; Chen and Ding 2012; Cong *et al.* 2013; ElHaddad *et al.* 2013). However, irreversibility also can be attributed to other effects, such as polymerization and covalent bonding to the surface of the adsorbent (Terzyk 2003a,b), as will be discussed next.

### Covalent Reactions of the Adsorbate

As just mentioned, one way to account for unexpectedly depressed extents of desorption, in cases where the bulk concentration of adsorbate is reduced, is to suppose that a reaction has taken place to render the compound insoluble. Several research teams have reached the conclusion that phenolic compounds may become covalently coupled to suitable carbonaceous surfaces (Magne and Walker 1986; Grant and King 1990; Ferro-Garcia *et al.* 1996; Vidic *et al.* 1997; Juhasz *et al.* 2002; Namasivayam and Kavitha 2003; Salame and Bandosz 2003; Terzyk 2003a; Moreno-Castilla 2004; Alvarez *et al.* 2005). Results reported by Mathialagan and Viraraghavan (2009) are also consistent with covalent bonding as a possible mechanism. Grant and King (1990) quantified such bound phenolic-based compounds by extracting the activated carbons with a variety of different solvents; the portion that could not be removed was considered to have been covalently reacted. Moreno-Castilla (2004) likewise found that a portion of adsorbed phenols could be removed from activated carbon surfaces by heating, whereas another portion could not. Terzyk (2003a) used thermogravimetric analysis and concluded that the covalently bound phenol-derived material was of minor amount. Vidic *et al.* (1997) and Uranowski *et al.* (1998) observed that the binding of phenolics to activated carbon was promoted by the presence of molecular oxygen. Figure 11 illustrates a mechanism that was proposed by Osei-Twum *et al.* (1996) to account for such coupling.

Though the reaction is shown in Fig. 11 as occurring between a pair of isolated monoaromatic phenol molecules, one could readily apply such a model to other situations, such as when a phenolic group is associated with the surface of an activated carbon product. Indeed, oxidative coupling of phenols appears to be enabled by oxygen-containing groups at the surface of suitably treated activated carbons (Alvarez *et al.* 2005). Salame and Bandosz (2003) proposed an esterification between the phenolic group and carboxyl groups at the carbon surface. Magne and Walker (1986) found that it was possible to avoid what they called “chemisorption” of phenol to activated carbon by minimizing both the contact time and temperature of exposure of the phenol to the adsorbate. An analogous oxidative coupling reaction also can take place in the presence of chlorine (Voudrias *et al.* 1985); however, the cited work warned of the likely formation of chlorinated phenols when carbon products are exposed to residual chlorine in water.



**Fig. 11.** Reaction scheme for oxidative coupling of phenols, forming dimers and larger species that presumably have much lower solubility in water. Scheme redrawn based on a concept by Osei-Twum *et al.* (1996).

Another possibility is that the phenolic compounds react among themselves, giving rise to oligomeric species having very low solubility (Vidic *et al.* 1994; Leng and Pinto 1997; Uranowski *et al.* 1998; Terzyk 2003a,b). Ravi *et al.* (1998) proposed that the adsorbed species undergo “chemical transformations”, making them more difficult to desorb. Vidic *et al.* (1994) and Uranowski *et al.* (1998) concluded that polymerization of phenolic compounds took place in the solution phase and was not affected by the presence of activated carbon. Again, the cited studies gave evidence that molecular oxygen in solution promoted the reaction.

### Kinetic Aspects of Adsorption

The kinetic aspects of adsorption of petrochemicals onto cellulose-derived adsorbents are generally the same as has been earlier discussed in reviews dealing with the biosorption of heavy metal ions and dyes (Hubbe *et al.* 2011, 2012). One important difference is that in the case of petrochemical compounds, the compilation in Table A reveals a much greater emphasis on activated carbon products. Thus, the microporous and mesoporous nature of activated carbon products merits particular attention here in terms of explaining rates of adsorption of petrochemical compounds.

#### *Pseudo-first-order model*

Several sets of investigators have reported good fits of adsorption data to a pseudo-first-order kinetic model (for instance Aber *et al.* 2009; Agarry *et al.* 2013). Many more examples can be found by inspection of Table A, where such behavior is denoted by “1<sup>st</sup>” in the column headed by “Rate law best fit”. Of all the theoretical models that have been used to fit adsorption data, perhaps the pseudo-first-order model is the most logical. To begin, it should be noted that the word “pseudo” is used because the concentration of adsorbate in the bulk of solution does not show up in the rate expression; presumably its value is high enough that it does not change appreciably during the experiment. Second, the term “first-order” implies that the rate of adsorption is always proportional to the number of unfilled adsorption sites, a value that decreases during the course of an



adsorption experiment. A typical expression for the pseudo-first-order model is given in Eq. 4 (Lagergren 1898; Arslan and Dursun 2008),

$$dq/dt = k_1 (q_e - q) \quad (4)$$

which can be integrated to arrive at the following expression:

$$\ln(q_e - q) = \ln q_e - k_1 t \quad (5)$$

In these expressions  $q$  indicates the amount of adsorbed compound per unit mass of adsorbate,  $t$  is the duration of exposure,  $q_e$  is the equilibrium amount of adsorption, and  $k_1$  is the pseudo-first-order rate constant.

In terms of what happens at a molecular level, the fact that a set of data fits well to a pseudo-first-order model implies that the unfilled sites at the surface are essentially equivalent to each other in terms of accessibility and that they remain so throughout the course of the experiment. There are two corollaries to this interpretation. The first is that such systems do not display a significant tendency for more favorable sites to be filled first. The second is that adsorption of one adsorbate molecule does not appear to affect the subsequent adsorption in an adjacent site. As one can see from Table A, a great many of the surveyed articles reported good fits to the pseudo-first order model. However, many systems did not, so various other models have been considered.

#### *Pseudo-second-order model*

Table A shows that the data from a great many of the surveyed systems could be well fitted to a pseudo-second-order expression for the rate of adsorption (for example Fu *et al.* 2012b). But as soon as one attempts to understand the implications for such fits, a serious problem becomes apparent. That is, the usual assumptions underlying the model do not appear to be consistent with the physical situation. In the pseudo-second order model, the rate expression indicates that the rate of adsorption is proportional to the square of the un-filled sites. This relationship can be expressed in the form shown in Eq. 6 (Ho and McKay 1999).

$$dq_t / dt = k (q_e - q_t)^2 \quad (6)$$

In Eq. 6,  $q_t$  is the amount of the compound adsorbed at time  $t$ ,  $k$  is the rate constant, and  $q_e$  is the amount adsorbed at equilibrium. After integration and rearrangement, the following form is obtained:

$$(t / q_t) = 1/(k_2 q_e^2) + (1/q_e)t \quad (7)$$

The usual way to interpret a good fit of data to such a rate expression is to assume that the rate-limiting step involves a tri-fold collision, such that the transition state involves one adsorbate molecule and two independent adsorption sites. But in cases where the adsorption sites are bound a solid surface, such an explanation lacks internal consistency. Because the sites bound on the adsorbent are unable to move independently of each other,

they cannot join in such a three-membered transition state. Thus, the usual way to account for pseudo-second-order rate behavior needs to be abandoned.

Fortunately, there is an alternative way to account for good fits of adsorption data to a pseudo-second-order rate expression. As first proposed in an earlier review article in this series (Hubbe *et al.* 2012), one relaxes the assumption that all adsorption sites have equal accessibility to adsorbate molecules. Instead, one assumes that the more easily occupied sites tend to fill up first, and the later sites become increasingly slower to be filled. Possible contributions to the slower filling of later-to-be-filled sites might be due to a wide range of circumstances, including the chemical nature of the site, the location of a site deeper within a narrow pore structure, or a degree of repulsion between already-adsorbed molecules and yet-to-be adsorbed molecules. The form of Eq. 7 is such that the deceleration in the rate of adsorption becomes increasingly severe as the surface approaches 100% saturation. The fact that the pseudo-second-order expression gives good fits to so many sets of data seems to be telling us that strong non-uniformity of accessibility or affinity of adsorption sites is the norm, rather than the exception, especially with respect to the last-to-be-filled sites.

To be consistent with the explanation just given, it is proposed that the pseudo-second-order rate expression be regarded as an empirical expression, very much in the same manner as the Freundlich adsorption isotherm has been regarded as being mainly a means to summarize experimental data (Freundlich 1907; Cal *et al.* 1994; Furuya *et al.* 1997). It is recommended that careful research be undertaken, with a focus on pure systems with well-defined pore structures, to shed more light on the underlying causes of pseudo-second-order adsorption rate behavior.

#### *Intraparticle diffusion*

Another model that has been very widely employed to fit and to interpret data for adsorption of petrochemicals onto cellulose-related adsorbents is the so-called intraparticle diffusion model (Webber and Morris 1963). Figure 12 provides a schematic view of the situation assumed in such cases. As shown, one envisions two possibilities for the rate-limiting step in adsorption, including (a) diffusion across a boundary layer at the outer surface of the particle of adsorbent material, and (b) diffusion within the particle.

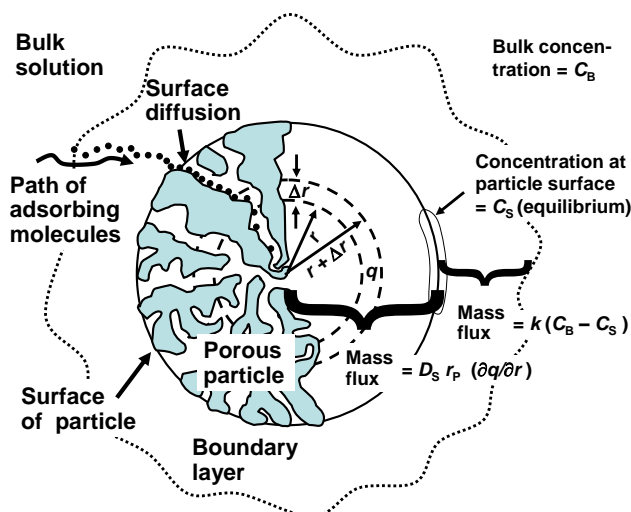
Webber and Morris (1963) considered cases in which the rate-limiting step appeared to be controlled by an activation energy. Presumably the activation energy is needed to cause momentary release of an adsorbate molecule from a surface site so that it is free to diffuse to an adjacent unoccupied site (either via surface diffusion or through the aqueous phase within the pore). Thus the rate of adsorption follows an Arrhenius relationship of the form,

$$k = A e^{-E/RT} \quad (8)$$

where  $A$  is sometimes called the frequency factor,  $E$  is the activation energy for adsorption,  $R$  is the gas constant, and  $T$  is absolute temperature.

Webber and Morris (1963) proposed that such a factor, in combination with a first-order model (essentially that of the pseudo-first-order model discussed earlier), could account for adsorption rates that were mainly controlled by rates of diffusion of adsorbate molecules from the outsides of finely porous activated carbon particles into their interiors.

The equation has been validated by carrying out experiments with different particle sizes of activated carbon (Webber and Morris 1963; Namasivayam and Sangreetha 2006; Zheng *et al.* 2010).



**Fig. 12.** Schematic diagram representing two potential rate-determining processes, including external diffusion and intra-particle diffusion (redrawn based on a concept from Hand *et al.* (1983) as discussed by Slaney and Bhamidimarri (1998).

The amount of adsorption can be expressed as a function of the square-root of time as (Aksu and Kabasakal 2005),

$$q = f [ D t / r_p^2 ]^{0.5} = K t^{0.5} \quad (9)$$

where  $f$  is a fitting parameter related to the activation energy,  $D$  is the effective diffusion constant of the adsorbate molecules within the finely porous particle,  $t$  is time duration,  $r_p$  is the radius of the porous particle of adsorbent, and  $K$  is the intraparticle diffusion rate constant.

The following studies found good to excellent fits of the intraparticle diffusion equation to their adsorption rate data (Mohan *et al.* 2005; Akhtar *et al.* 2009). The activation energies computed from the intraparticle diffusion model sometimes have been used as a basis for deciding if the term “physisorption” or “chemisorption” is more appropriate in a given case (Allen *et al.* 2005).

#### Other kinetic models

Several additional kinetic models are worthy of note, since research teams have found that they sometimes achieve better fits to data, compared with the models already mentioned. Selected examples of such studies and kinetic models are listed and described in Table 5.

**Table 5.** Selected Examples Where Other Rate Equations Were Used to Account for Adsorption of Petrochemicals onto Cellulose-derived Adsorbents

Model and its Attributes	Citation
<b>Surface diffusion.</b> A model is presented for cases in which the rate of diffusion of sorbate as it progresses in two dimensions across the surface of an adsorbent is a function of the degree of saturation. Presumably, as the surface sites become filled, diffusion becomes greatly restricted.	Chatzopoulos <i>et al.</i> 1994; Chatzopoulos and Varma 1995; Karimi-Jashni and Narbaitz 1997
<b>Saturation-type kinetics with film and intraparticle diffusion.</b> This type of model was used to interpret rates of pesticide adsorption onto powdered activated carbon. A good fit to this type of model implies that at least part of the process does not depend on the concentration of adsorbate in the bulk solution; the concentration-independent factor might involve the diffusion of adsorbate as a film at the surface of pores in the adsorbent.	Aksu 2002; Aksu and Kabaskal 2005
<b>Pseudo-second-order rate with evidence of intraparticle diffusion control.</b> Though Morris and Webber (1963) did not consider use of the pseudo-second-order rate model when proposing the “intraparticle diffusion” theory, other authors have shown that such an approach can make sense. Good fits to such a combination of models seem to imply that there is an activation energy involved (perhaps related to the energy required to cause an adsorbate molecules to jump from one site to an adjacent site somewhat deeper in the adsorbent), and that sites differ significantly with respect to their favorability for adsorption.	El Bakouri <i>et al.</i> 2009
<b>Boyd plot.</b> Data are plotted in such a way as to determine whether the rate of adsorption is controlled by intraparticle diffusion or by mass transfer at the surface of the adsorbent.	Boyd <i>et al.</i> 1947; Aravindhan <i>et al.</i> 2009
<b>Bangham’s equation.</b> A linear fit to the equation provides evidence that the slow step in adsorption involves diffusion into pores.	Gupta and Ali 2008; Gupta <i>et al.</i> 2011
<b>Elovich equation.</b> The model assumes an exponential decrease in the rate of adsorption with increasing adsorbed amount. The model may imply that the remaining sites are less and less accessible. Alternatively, the presence of adsorbed molecules may impede diffusion to the more deeply located sites.	Wu and Tseng 2006
<b>Plots of adsorption vs. square root of time.</b> In principle, if such a plot shows more than one linear section, then one may conclude that adsorption is controlled by parallel processes occurring at different rates. The cited work by Ioannou and Simitzis (2009) was particularly ambitious in such an approach, making a case for four different regions of the curve. Such findings will require more critical evaluation, since not all transport mechanisms give rise to a dependency of adsorbed amount on the square root of time.	Juang <i>et al.</i> 1996a; Singh <i>et al.</i> 2008; Ioannou and Simitzis 2009; Ofomaja 2011; Ofomaja and Unuabonah 2013
<b>Shrinking core model.</b> A careful analysis of adsorption onto sphere-like porous particles needs to consider how the adsorbate may diffuse as a “front”, which gradually decreases the remaining diameter of a shrinking core in which adsorption sites are still not filled.	Lang <i>et al.</i> 2009
<b>Retarded diffusion.</b> It has been found useful to define a retarded diffusion constant when considering transport of adsorbate into relatively large, dense materials such as wood chips.	Mackay and Gschwend 2000
<b>Slow steps in adsorption.</b> The cited authors focused on diffusion limitations posed by natural organic matter matrices and extremely fine pores.	Pignatello and Xing 1996

<b>Divergence between adsorption rate and capacity.</b> The cited authors reported that the highest rate of adsorption did not coincide with the highest capacity. Such findings are generally consistent with the idea that micropores within activated carbon are the most difficult to access, and they also have the highest surface area for adsorption.	Roostaei and Tezel 2004
<b>Half-life, half-capacity approach.</b> This analysis, based on a Langmuir isotherm model and a pseudo-second-order rate of adsorption, revealed a case in which a lower capacity adsorbent was more effective for packed-bed applications, requiring fewer stages of treatment.	Tseng <i>et al.</i> 2011
<b>Adsorbate's diffusivity in the substrate's partition phase.</b> Fast and slow rates of adsorption can be accounted for by a model in which adsorption first takes place onto a "partition phase", from which release into other parts of the adsorbent is relatively slow.	Chen <i>et al.</i> 2012b

### Interpretation of Packed Bed Results

Much of the emphasis, up to this point in the article, has been on studies focused on quasi-equilibrium conditions. Indeed, most of the studies represented in Table A can be described as batch-type adsorption experiments. But important research also has been carried out with continuous flow-through systems, *i.e.* packed beds (Gupta *et al.* 2000; Garcia-Mendeita *et al.* 2003; Gupta and Ali 2008; Rossner and Knappe 2008; Hank *et al.* 2010). Such studies provide an essential link to some of the most promising scale-up opportunities for biosorption technologies.

A key goal of studies involving packed beds has been to accurately predict breakthrough – often defined by the point in time at which the concentration of contaminant at the outlet of the column reaches half of its value at the inlet (Slaney and Bhamidimarri 1998; Chern and Chien 2002, 2003; Chuang *et al.* 2003a,b; Akzu and Gönen 2004; Rossner and Knappe 2008; Wu and Yu 2008; Sulaymon *et al.* 2012; Zeinali *et al.* 2012). Researchers also have been concerned with the steepness of the breakthrough curves (Brasquet *et al.* 1996; Brás *et al.* 1999), a factor that affects the degree to which the capacity of the adsorbent can be utilized before the concentration of pollutant in the outlet stream becomes unacceptably high. The concentration distribution in a column also can be used as the basis for estimation of rates of adsorption, as well as diffusion rates (Wolborska 1989).

In principle, since continuous flow experiments do not provide time for equilibration, one might expect such experiments to reveal lower adsorption capacities in comparison to batch-type types. However, the opposite has been reported in a couple of cases (Tyagi and Srivastava 1996; Gupta *et al.* 2000). Thus, there is reason to more closely consider some theoretical aspects.

In terms of modeling, there appears to be general agreement that the breakthrough curve can be estimated from an equation of the form,

$$\varepsilon \frac{\partial C}{\partial t} + u_o \varepsilon \frac{\partial C}{\partial z} + \rho \frac{\partial q}{\partial t} = 0 \quad (10)$$

where  $\varepsilon$  is the void volume,  $C$  is the local concentration of pollutant in solution,  $t$  is the elapsed time since the start of elution,  $u_o$  is the interstitial flow velocity,  $z$  is the distance from the inlet of the packed bed,  $\rho$  is the density of solid (carbon) in the packed bed, and

$q$  is the local concentration of pollutant in the stationary phase (Chern and Chien 2002). The cited article gives a good description of the assumptions and boundary conditions that are used when applying the equation. Through use of various simplifications, the elution time can be expressed in the following form,

$$t = t_{1/2} + \frac{\rho q_F}{\varepsilon K_L a C_F} \int_{C_F/2}^C \frac{1}{C - g\left(\frac{q_F C}{C_F}\right)} dC \quad (11)$$

where  $t_{1/2}$  is the time at which the dimensionless effluent concentration equals 0.5, the subscript “F” stands for “feed”,  $a$  is the mass transfer area per unit volume of the bed, and  $g$  is the mobile phase concentration at equilibrium.

In order to make predictions related to breakthrough curves it is necessary to input information about adsorbed amounts as a function of local concentration. This is usually done with use of the Langmuir model, or some other suitable model, to express the adsorption isotherm. In the case of the Langmuir model, the following equation can be used to relate elution time to other variables (Chern and Chien 2002),

$$t = t_{1/2} + \frac{\rho N}{\varepsilon K_L a C_F} \left\{ \ln 2x + \frac{1}{1 + KC_F} \ln \frac{1}{2(1-x)} \right\} \quad (12)$$

where  $N$  and  $K$  are Langmuir parameters (mol/kg and m<sup>3</sup>/mole, respectively) and  $x$  is the normalized effluent concentration, *i.e.* the local concentration divided by the feed concentration (dimensionless).

Various aspects of the predictions of models have been confirmed in studies of adsorption of petrochemicals onto cellulose-derived adsorbents (Wolborska 1989; Chuang *et al.* 2003a; Gupta and Ali 2008; Rossner and Knappe 2008; Hank *et al.* 2010; Zeinali *et al.* 2012). For example, it has been found that the efficiency of uptake tends to fall when the flow rate is increased (Aksu and Gönen 2004; Wu and Yu 2008). Effects of the size of porous particles have been quantified (Garcia-Mendieta *et al.* 2003). Chern and Chien (2002, 2003) showed that the breakthrough performance could be envisioned based on constant wave patterns of solute concentrations progressing through a bed. Sulaymonn *et al.* (2012) predicted breakthrough curves using a model based on external and internal mass transfer, with provision for axial dispersion. Slaney and Bhamidimarri (1998) were able to account for breakthrough curves by assuming a surface diffusion model of the adsorbate within the particles of activated carbon. Brasquet *et al.* (1996) observed a strong selectivity, with ready adsorption of the small hydrophobic molecules phenol and atrazine, but very inefficient adsorption of high-mass humic substances.

One of the odd consequences of data fitting is that the value obtained for maximum adsorption, based on a fitting of data from packed bed experiments, is sometimes higher than what has been obtained for the same systems when batch adsorption tests were carried out (Tyagi and Srivastava 1996; Gupta 2000). Such findings are unexpected due to the fact that batch experiments allow much more time for adsorption to approach equilibrium. A possible explanation for the seemingly reversed results is that different ranges of input data are often used in such pairs of analyses. The packed bed experiments seldom incorporate data corresponding to nearly full saturation. As a consequence, the fitting of a value for

maximum adsorption inherently involves an extrapolation somewhat beyond the range of the actual data, especially in the case of data from dynamic testing in a packed bed.

### **Biodegradation Aspects**

Another factor that can affect not only the rate but even the amount of petrochemical compounds removed from water in the presence of cellulose-based materials is biodegradation. Biodegradation is also considered in parts 2 and 3 of this series of articles, which deal with the removal of dyes and liquid oils from water (Hubbe *et al.* 2012, 2013). As has been pointed out in some review articles, various petrochemical compounds can be effectively degraded by the enzymatic action of bacteria and fungi (Juhász and Naidu 2000a; Bamforth and Singleton 2005; Julinová and Slavík 2012). However, as noted by Julinová and Slavík (2012), the process of biodegradation under ambient conditions often requires a long time.

Several teams of researchers have presented evidence that biodegradation can play a significant role as a process that goes on in parallel to biosorption (Dec and Bollag 1994; Ha and Vinitnantharat 2000; Lei *et al.* 2002; Raghukumar *et al.* 2000b; Kliaugaitė *et al.* 2008; Liu *et al.* 2009; Oh *et al.* 2011; Chen and Ding 2012; Hai *et al.* 2012; Ding *et al.* 2013; Senkaran *et al.* 2013; Ye *et al.* 2013). For instance, Dec and Bollag (1994) noted that peroxidases were able to detoxify water that was contaminated with phenolic compounds. Most notable are studies in which the decomposition products from biodegradation of petrochemical compounds were either detected or quantified (Tsezos and Wang 1991; Benoit *et al.* 1998; Sethunathan *et al.* 2004; Chan *et al.* 2006; Gao *et al.* 2011).

Liu *et al.* (2009) were able to distinguish between biodegraded alkanes and those that remained within bioflocs, a location that appeared to protect part of the alkanes from biodegradation. Such entrapment, meaning biosorption rather than just biodegradation, was observed after about 50 to 60 hours of bacterial culturing. Chen *et al.* (2010) found evidence that biosorption tended to inhibit biodegradation by white-rot fungi. Similar findings were reported by Pignatello and Xing (1996) for various organic compounds, and Wang and Grady (1995) found the same in the case of di-n-butylphthalate. Stringfellow and Alvarez-Cohen (1999) concluded that although adsorption of polynuclear aromatic hydrocarbons onto bacterial biomass tended to suppress their biodegradation in the short run, the pollutants may be ultimately degraded in the longer term, and in any case the biosorbed hydrocarbons become removed from the water phase.

Seo *et al.* (1997) found that the ability of activated carbon to take up peptone and various other pollutants was increased by a factor of four after inoculation of the system with microorganisms. Hank *et al.* (2010) found that the ability of activated carbon to remove phenol from solution was greatly enhanced by the presence of a biofilm, and the effect was attributed partly to biodegradation. Likewise, Hu *et al.* (2013) and Li *et al.* (2013) demonstrated the effectiveness of activated carbon that had been “bioaugmented” with bacterial films for the removal of methyltert-butyl ether (MTBE) from soil samples. The growth of degrading organisms as a biofilm on the carbon particles provided the capability of long-term removal of MTBE, making it unnecessary to replace or otherwise reactivate the adsorbent.

Various researchers have used microbes to decompose adsorbed petrochemicals, thereby restoring the adsorptive capacity to activated carbon (Vinitnantharat *et al.* 2001). Ivancev-Tumbas *et al.* (1998) used aerobic microbial treatment to achieve regeneration of

activated carbon that had been used for the adsorption of phenol. Oh *et al.* (2013) used biodegradation to regenerate activated carbon that had become loaded with 4-chlorophenol. Toh *et al.* (2013) found that granular activated carbon could be regenerated after having been loaded with phenol and o-cresol, by exposure to microbial cultures. Sodha *et al.* (2013) achieved only about 58% of regeneration of the adsorption capacity of activated carbon for phenol after bacterial culturing to degrade the phenol. Oh *et al.* (2011) found that biofilm-coated activated carbon particles were effective in degrading chlorophenols only when the concentration of the pollutant was at or below the level to which the microorganisms had become acclimatized. Romeh (2010) found that inoculation of water with certain bacteria resulted in a drastic decrease in the pesticide imidacloprid within 48 h, whereas a much lesser change was observed in parallel experiments with the same biomass in suspension, but without inoculation. Samanta *et al.* (2002) noted that although naturally occurring bacteria can break down many polycyclic aromatic compounds, their performance may be improved by metabolic engineering.

In some other cases the authors concluded that most of the removal of the petrochemical compounds was attributable to biosorption rather than biodegradation (Augulyte *et al.* 2009; Namane *et al.* 2012). To add some perspective, it should be recalled from an earlier part of this article that many researchers found little or no advantage of utilizing live micro-organisms, rather than heat-killed microbial biomass of the same type as a means of removing the petrochemicals from solution (Yan and Allen 1994; Lei *et al.* 2002; Chen *et al.* 2010; Ding *et al.* 2013), and in a few cases the dead biomass was found to be more effective (Wang and Grady 1994; Lang *et al.* 2009).

Another factor that can help put matters into perspective is to compare the times required to get rid of a target pollutant; for example, while most of the studies represented in Table A indicate that most of the biosorption took place within the first hour, a study by Chen and Ding (2012) found that three days was required to decrease the phenanthrene content of soil by 20 to 40%, and 90 days was needed to reduce the amount by 60 to 95% in the presence of various bacterial or fungal cultures. Similar results were reported by Gao *et al.* (2011) for nonylphenol and biosorption and/or biodegradation by *Chlorella* species. Also Lei *et al.* (2002) found that pyrene was first adsorbed onto live microbial cells and then more gradually biodegraded, with the rates differing for different micro-organisms and conditions. Sethunathan *et al.* (2004) found that algae were effective for relatively quick biosorption of an endocrine disrupting insecticide from water, allowing most of it to be biodegraded within 10 to 50 days, depending on the details.

## LIFE CYCLE ISSUES

Up to this point in this article the relative success of biosorption has been mainly considered in terms of adsorption capacities and rates. But full success of a biosorption process also requires that an approach is cost-effective, that each step fits well with the next in an integrated program, and that potential adverse environmental impacts are avoided or minimized. Some aspects of environmental impacts will be considered here, with attention to the possible fate of cellulose-based absorbent material after it has been used to collect various petrochemical compounds from water. For instance, it has been pointed out that the production of the adsorbent material itself will ideally be carried out in



an environmentally friendly way, with preference given to bio-based, photosynthetically renewable materials (Ali *et al.* 2012). Because some of these same issues already were covered in an earlier review article (Hubbe *et al.* 2013), the discussion that follows is somewhat abbreviated.

### Practical Handling of Particulate Matter

As has been mentioned in an earlier review article (Hubbe *et al.* 2011), relatively large particle or fibers of adsorbent material are likely to be advantageous in term of practical handling. In batch operations relatively large particles are more easily collected, and in packed bed systems they may provide less resistance to flow. But again when considering adsorption of petrochemical compounds, little research could be found dealing with such practical issues. As an exception, Han *et al.* (2013) showed that activated carbon could be rendered ferromagnetic by incorporation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles. Khoshmood and Azizian (2012) likewise prepared activated carbons having magnetic properties. Such materials could be easily removed from solution by use of a magnet. It is worth noting that such issues were hardly mentioned in the great majority of articles considered in this review. Once again, the paucity of research concerning various highly practical issues implies that there remain critical needs for academic and industrial research by engineers and scientists in the coming years.

### Regeneration

The philosophy behind regeneration is that the biosorbent ought to be used multiple times, thus minimizing any environmental costs associated with its preparation. Once the biosorbent material has become loaded with the target pollutant or pollutants, there ought to be a benign way to remove the target compounds and to restore the adsorbent near to its initial state and capacity. As proposed by Pollard *et al.* (1992), it would be most desirable for such regeneration to be carried out *in situ*, thus allowing a packed bed of the adsorbent to be used multiple times. Several approaches to accomplish this are considered in the subsections that follow.

#### *Regeneration by rinsing with an organic solvent*

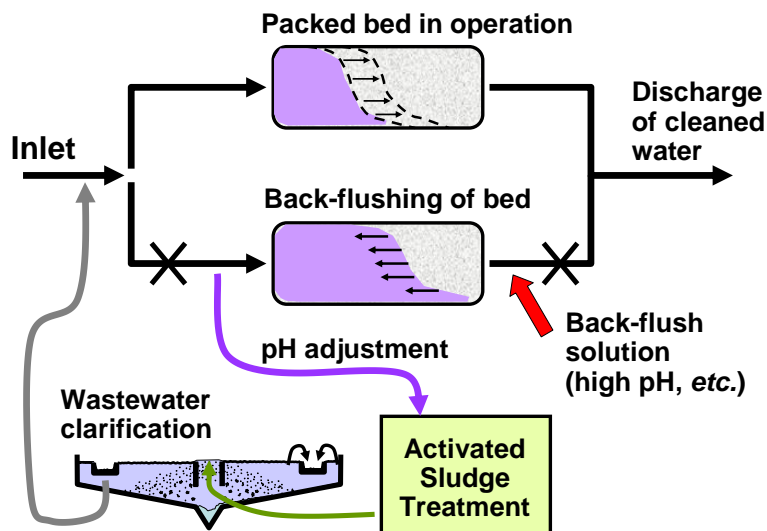
In principle it would be possible to restore many adsorbents by a kind of dry-cleaning, essentially rinsing them off with an organic solvent (Srivastava and Tyagi 1995b; Ferro-Garcia *et al.* 1996; Leng and Pinto 1997; Gupta *et al.* 2000; Juhasz and Naidu 2000b; Denizli *et al.* 2004, 2005; Akhtar *et al.* 2007b; Sathishkumar *et al.* 2008; Stasinakis *et al.* 2008; Lang *et al.* 2009; Tan *et al.* 2009a,b). However, there is reason to doubt that such approaches make sense in terms of environmental impact. While the adsorbent may become cleaned, the solvent becomes contaminated. A possible exception to this rule is that sometimes it is possible to use adsorption as a means to pre-concentrate organic liquids as a step towards obtaining them in their pure form (Aktar *et al.* 2007a). In general, however, it makes sense to seek alternatives to the use of organic solvents in the regeneration of adsorbents.

#### *Release back into an alkaline aqueous phase as a concentrate*

When dealing with phenolic compounds many researchers have observed that it is possible to transfer much of the adsorbed material back into aqueous solution by raising

the pH to approximately 10 or 11 or higher (Leng and Pinto 1997; Tyagi *et al.* 1997; Akhtar *et al.* 2009; Anirudhan *et al.* 2009; Gupta *et al.* 2000; Kujawski *et al.* 2004; Özkaya 2006; Tang *et al.* 2007; Kumar 2009b; Kumar and Min 2011b; Abdallah 2013). Brandt *et al.* (1997) found that raising the pH to 7 was sufficient to regenerate bacterial biomass that had been loaded with pentachlorophenol; such results are consistent with the much stronger acidity of that compound in comparison to most other phenols. Chularueangaksorn *et al.* (2013) employed a mixture of NaOH and NaCl in a methanol-water (70:30) solution to remove perfluorooctane sulfonate from an anionic exchange resin. Presumably the regeneration by base should be performed with a minimum of aqueous phase, such that the resulting aqueous solution is many times more concentrated than the original polluted water. Leng and Pinto (1997) found that oxygen-free conditions were much more effective than oxygenated conditions when using a methanol-NaOH combination to remove phenol from activated carbons. Treatment with alkaline solution also has been found to be effective for regeneration of activated carbons that had been loaded with certain other contaminants, such as pesticides (Hamadi *et al.* 2004). In work that calls into question the need to always raise the pH of the desorbing solution, Wu and Yu (2007, 2008) found that simple equilibration with deionized water was able to remove over 80% of adsorbed 2,4-dichlorophenol from fungal beds; however such easy desorption may raise concerns regarding insufficient affinity in those cases between the target adsorbate and a candidate adsorbent to achieve effective removal in the first place.

Figure 13 describes a possible scheme that might be employed to treat the concentrated rinsate from an alkaline regeneration operation. After pH adjustment, it is proposed that the mixture be subjected to biological treatment with activated sludge in conventional wastewater treatment systems or bioreactors (Farhadian *et al.* 2008; Kwon *et al.* 2011; Al-Khalid and El-Naas 2012; Niti *et al.* 2013).



**Fig. 13.** Schematic diagram of a scheme for desorptive regeneration of a packed bed, followed by biodegradation of the rinsate, and then recapture of any remaining contaminant onto the packed bed, allowing release of purified water

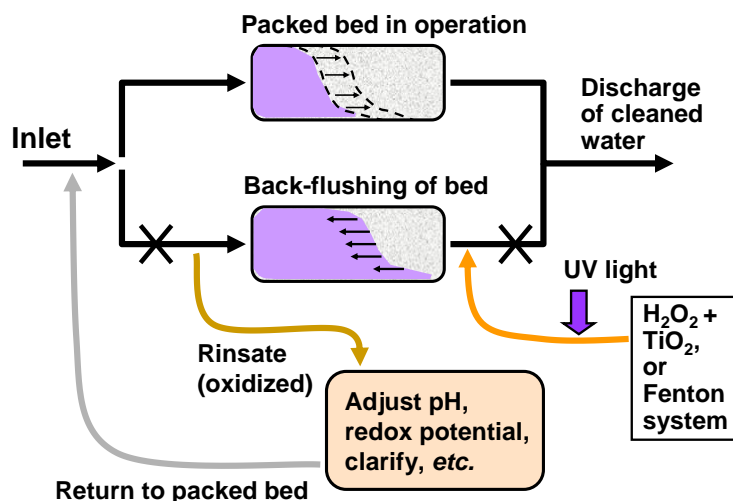
Note that according to the diagram the biologically clarified water is then sent once again through the packed bed system. Incorporation of such a repetition of biosorption is justified by the presumed low rates of biodegradation of many petrochemical products. On the other hand, it can be expected that an activated sludge system can become increasingly effective in biodegradation during repeated cycles due to the enrichment of microbes in the activated sludge that are capable of breaking down various recalcitrant compounds.

### *Oxidative degradation*

Another promising approach to the regeneration of a contaminated adsorbent material can involve oxidation or bleaching, with the aim of breaking down the adsorbed compounds into non-harmful byproducts. Such an approach depends both on the nature of the adsorbed compounds and the type of oxidant. Compared to the biological processes just described, oxidative processes can be quite rapid, offering the possibility of *in-situ* regeneration of packed beds.

Advanced oxidation processes (AOP) are of particular interest relative to their possible use in the regeneration of packed beds contaminated with hard-to-oxidize compounds (Pera-Titus *et al.* 2004; Pignatello *et al.* 2006). For instance, such processes can employ a combination of UV light and an oxidant such as  $\text{H}_2\text{O}_2$  to generate  $\text{OH}^\bullet$  radicals. Another approach is to use Fenton's reaction, wherein  $\text{Fe(II)}$  is used with  $\text{H}_2\text{O}_2$  to generate such radicals. Much less is known regarding possible scale-up of such processes for in-situ treatment of packed beds. Doocey and Sharratt (2004) showed that a Fenton catalysis system could be used to regenerate zeolite that had been contaminated with chlorophenols. Chan *et al.* (2007) employed photocatalytic oxidation for the treatment of seaweed that had been used to adsorb di(2-ethylhexyl)phthalate. Titanium dioxide particles were employed as a catalyst along with hydrogen peroxide as the oxidant and ultraviolet light to initiate the reaction. Complete regeneration was achieved within 45 min under optimum conditions. Okawa *et al.* (2007) achieved similar results using wet peroxide oxidation to remove trichloroethylene from activated carbon. Apparently the activated carbon itself was able to play the role of catalyst, causing  $\text{H}_2\text{O}_2$  to decompose, yielding the desired  $\text{OH}^\bullet$  radical. Some loss of adsorption capacity was observed, and this was attributed to partial oxidation of the adsorbent. Omri and Benzina (2014) generated very small anatase  $\text{TiO}_2$  particles onto the surface of activated carbon particles; such systems made it possible to first adsorb phenol, then subject it to photocatalytic oxidation.

Figure 14 provides a schematic diagram suggesting how an advanced oxidation treatment could be integrated into a packed bed system for the removal of oxidizable petrochemical compounds from water. As shown, once the packed bed has reached its capacity, the concept is to backflush the system in such a way that the derived oxidative radical species are in their active form and able to interact with the adsorbed contaminants. Because the packed bed material presumably will be opaque to ultraviolet light, there are various research questions that need to be answered. For instance, the limited lifetimes of radical species may make it difficult to optimize the oxidation of compounds held within the adsorbent material.



**Fig. 14.** Schematic diagram of a concept for *in-situ* oxidative regeneration of a packed bed that has been used for the adsorption of petrochemical compounds

#### *Thermal regeneration*

The idea behind thermal regeneration is to employ conditions similar to, but generally milder than those used in the initial preparation of activated carbons. Basically, one heats the material in the absence of oxygen such as to cause desorption of the collected organic molecules and restoration of the pristine conditions within the mesopores and micropores of the carbon (Moreno-Castilla *et al.* 1995a; San Miguel *et al.* 2001; Denizli *et al.* 2004; Sabio *et al.* 2004; Namasivayam and Sangreetha 2006; Maldonado-Hódar *et al.* 2007; Stasinakis *et al.* 2008; Román *et al.* 2013). Román *et al.* (2013) attributed the observed desorption to thermal removal of functional groups from the carbon surface, as well as cracking of the chemisorbed compounds. Álvarez *et al.* (2004, 2009) found that an additional 15% of mass loss from the carbon was incurred during heating at 1123 °K with carbon dioxide gas to restore activated carbon that had been used to adsorb phenol. It was found that similar results could be obtained with ozone gas treatment at room temperature (Álvarez *et al.* 2005, 2009). Sabio *et al.* (2004) found that gasification with carbon dioxide was much more effective than simple pyrolysis in the regeneration of active carbon loaded with *p*-nitrophenol. Ania *et al.* (2005) found that microwave heating made it possible to achieve more rapid regeneration of activated carbon with less harmful effect on the pore size distribution than conventional heating. San Miguel *et al.* (2001) found that steam gasification was very effective for regeneration of activated carbon, but that excessively severe conditions deteriorated the microporosity of the adsorbent.

#### *Biological regeneration or treatment*

Adsorbent material also can be regenerated by exposing it to conditions that allow biological decomposition (Ivancev-Tubas *et al.* 1998; Vinitnantharat *et al.* 2001; Oh *et al.* 2013; Sodha *et al.* 2013; Toh *et al.* 2013). For instance Ivancev-Tubas *et al.* (1998) employed aerobic conditions that allowed micro-organisms to break down adsorbed phenol on activated carbon. A study by Oh *et al.* (2013) revealed no effect of the amount of adsorbed chlorophenol on the bioregeneration of activated carbon. Sekaran *et al.* (2013)

immobilized bacteria on activated carbon to decontaminate sulphonated phenolic compounds. On the other hand, Toh *et al.* (2013) found that it made no difference whether microbial biomass was immobilized or free-floating during the bioregeneration of activated carbon loaded with phenol and *o*-cresol.

One of the key concerns about the kind of approach just mentioned is that biodegradation may be too slow for practical use in many packed bed systems. A possible way to get around this dilemma is to allow biodegradation to take place continuously within the bed. Examples employing of such an approach were mentioned earlier (Hu *et al.* 2013; Li *et al.* 2013c). A challenging aspect of such an approach is the need to maintain conditions is a suitable range for biological growth, possibly including control of pH, temperature, and micronutrients. While the cited studies claimed success for semi-continuous biosorption and biodegradation of some selected contaminants, more such research is needed to determine if the concept can be scaled up and used for diverse and variable streams of contaminated water.

In addition to considering use of biodegradation as a way to recondition adsorbent material, one needs to appreciate that biodegradation constitutes a key step in conventional wastewater treatment programs. For instance, Al-Khalid and El-Nass (2012) have reviewed studies dealing with the aerobic biodegradation of phenols. Such treatment can be understood as involving adsorption of the pollutants onto bacterial sludge, in addition to the possibility of enzymatic breakdown while the target compounds are in the soluble phase. Several studies have documented the adsorption of phenolic compounds and other petrochemicals onto bacterial sludge of the type generated during wastewater treatment (Bell and Tsezos 1988, 1989; Tsezos and Wang 1991a,b; Kennedy *et al.* 1992; Yan and Allen 1994; Aksu and Yener 1998, 2001; Stringfellow and Avlarez-Cohen 1999; Karim and Gupta 2002; Aksu and Gönen 2004; Gao and Wang 2007; Thawornchaisit and Pakulanon 2007; Arslan and Dursun 2008; Augulyte *et al.* 2008; Ochoa-Herrera and Sierra-Alvarez 2008; Yu and Hu 2011; Julinová and Slavík 2012; Li *et al.* 2013b; Sulaymon *et al.* 2013). Pan *et al.* (2010) also documented the adsorption of phenanthrene to water-soluble polymeric substances released by bacterial sludge. These studies can serve as a reminder not to draw a sharp dividing line between biosorption and biodegradation processes. In fact, the two processes appear to be working in tandem during conventional wastewater treatment with the application of activated sludge.

### Life-Cycle Comments for the Series of Review Articles

Table 6 provides a summary of options for the handling of spent cellulose-based adsorbent materials corresponding to the contaminant classes considered in the four review articles in this series (Hubbe *et al.* 2011, 2012, 2013, and the present article). In this table the word “Yes” is used to indicate that the effectiveness of the proposed approach is at least partly supported by published articles. The question mark is used in cases where there is a serious need for more research. And the word “No” is used when the existing literature has revealed scant support for the given option. As can be seen, there are many question marks in the table. That’s good news for people who want to embark on a career to try to solve some of those problems. The table also exposes the seriousness of the challenge regarding commercial-scale implementation of concepts that already have shown promise in the laboratory.

**Table 6.** Tentative Rating of Possible Regeneration Schemes for Use with the Four Classes of Pollutants Considered in this Series of Articles

	Metals	Dyes	Oil	Petro-chem.
<b>REGENERATE THE ADSORBENT</b>				
Concentrate the rinsate.	Yes	No	No	No
Biodegrade rinsate & recirculate.	No	Yes	-?-	-?-
Chemically degrade <i>in situ</i> .	No	Yes	No	-?-
<b>INCINERATE FILLED ADSORBENT</b>				
Recover energy from biomass.	Yes	Yes	Yes	-?-
Recover concentrated adsorbate.	-?-	No	No	No
<b>LANDFILL (leaching concerns)</b>	-?-	Yes	No	No
<b>BIODEGRADATION OF ADSORBENT</b>				
Anaerobic (then recirculate)	No	Yes	-?-	-?-
Activated sludge water treatment	No	Yes	No	-?-
Composting (self-contained)	No	-?-	-?-	-?-

## CONCLUDING REMARKS

Based on the many scientific works that have been considered in this review, it is clear that there is a great deal of interest in using adsorbents based on cellulosic materials as a means to remove various petrochemical pollutants from water. However, full-scale implementation of this type of technology does not appear to have kept pace. According to Gadd (2009) as well as Fomina and Gadd (2014), there has been little or no industrial exploitation of plant-based adsorbent materials other than activated carbon products. To put a positive spin on this statement, however, there has been substantial progress in understanding the wide range of cellulose-based sources that can be used in the preparation of activated carbons, and progress has been made in understanding how to achieve favorable pore structures – achieving a good balance between high surface area and ready accessibility of internal sites for adsorption.

Activated carbon products generally can be described as being highly efficient adsorbents that can be fully combusted after their use, as one promising option. In addition, activated carbons loaded with various pollutants can be regenerated by such means as mild pyrolysis, microbial treatment, and by back-washing. Although back-washing with high-pH aqueous solution appears to be a good approach for removing non-covalently bound phenolic compounds from cellulose-based adsorbents, such an approach presupposes that a wastewater treatment facility is available and that it has adequate means of dealing with the highly polluted rinsate that results from such operations. One promising approach would be to subject such rinsate to biodegradation under controlled conditions, possibly using biosorption once again in a follow-up step to polish water before it passes from a wastewater treatment system to a natural waterway.

Though it is clear from the surveyed literature that a lot of progress has been made concerning the regeneration of spent adsorbent, it would appear that there should be a priority to develop even better systems for *in-situ* regeneration, with emphasis on

approaches that break down the contaminant rather than just transferring it to another phase. The published literature, as has been discussed in this article, already has shown substantial progress in this area, *e.g.* the *in-situ* oxidative treatment of the adsorbent (Chan *et al.* 2007; Okawa *et al.* 2007), or biodegradation of various compounds while they are mainly being held in place by activated carbon or other cellulose-derived adsorbents (Ivancev-Tubas *et al.* 1998; Vinitnantharat *et al.* 2001; Oh *et al.* 2013; Sodha *et al.* 2013; Toh *et al.* 2013). Research in this area needs to address a reported tendency for biosorption to suppress rates of degradation of the adsorbed species (Stringfellow and Alvarez-Cohen 1999; Liu *et al.* 2009). It would seem that a suitable balance of containment of the contaminant on the adsorbent material, while also allowing sufficient diffusion to enable the desired degradative processes to occur, could be achieved by varying such parameters as pH, temperature, and strategic uses of surfactants, among other variables.

If one's goal is to promote the usage of cellulose-based adsorbents, it would make sense to aim for applications that are likely to play to the strength of this type of technology. As noted by Moreno-Castilla (2004), the use of adsorbents is especially appropriate when there is a need to remove low concentrations of highly objectionable compounds from aqueous solution. Biosorption can be recommended as a polishing step after other wastewater treatment operations, such as pre-filtration, coagulative settling (primary clarification), and activated sludge (secondary wastewater treatment) have removed the major portion of contaminants. Relative to membrane-based separations, biosorption offers far fewer concerns about flow restrictions and fouling. Other options such as evaporation and fully effective reverse osmosis as means to purify water involve much higher cost per volume of water to be purified.

Finally, it would seem that the time is ripe for further exploitation of torrefied wood in certain applications calling for biosorption. One of the promising attributes of torrefied wood, compared to the source material, is its more hydrophobic character in comparison to the original plant material, especially following more severe levels of treatment (Ibrahim *et al.* 2013). As noted by Penmetsa and Steele (2012), there is potential to impart stronger hydrophobic character to torrefied wood by treating it with certain low-cost hydrophobic materials. Such treatment would likely increase the effectiveness of the material for removing various synthetic organic compounds from water. Compared to activated carbons, torrefied wood products offer potential advantages such as much higher yield (relative to the raw material), a well-developed, interconnecting macro-pore structure associated with fiber lumens, and a rich diversity of surface chemical groups, all attributable to the much lower level of thermal degradation in comparison to conventional activated carbons. A wide diversity of surface sites would tend to favor use of an adsorbent material for a broad range of potential applications. Thus it is hoped that when a similar review article is written ten years from now, some key developments in the field will include large-scale, economical preparation of torrefied biomass products that have been engineered for more effective use as adsorbents.

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## APPENDIX

**Table A.** Tabulation of Research Publications for Removal of Dissolved Petrochemicals from Dilute Aqueous Solution by Use of Raw or Modified Lignocellulosic Materials (See notes below table for key to abbreviations)

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Phenol	Brown algae, Macrophyta, Tea residue	Air dry	HCl 0.1 N	F (L)	0.04, 0.87 0.02	-	-	Favorable pH = 10; heterogeneous sites	Abdallah 2013
101 organic compounds	Activated carbon	-	-	-	-	-	-	Adsorption favored by C, Br, Cl in molecule. Decreased by O and H.	Abe <i>et al.</i> 1985
Phenol, <i>p</i> -Nitrophenol	Kenaf cloth act. C	AC	K <sub>2</sub> HPO <sub>4</sub> activ.	L, T	137-141	1 <sup>st</sup>	-	Activation conditions	Aber <i>et al.</i> 2009
Phenol and <i>o</i> -Cresol	Activated carbon (coal)	AC	-	L	100-300, 200-400	ID	-	Intraparticle diffusion is rate-limiting step.	Abuzaid & Nakhala 1994
Dichloromethane, CHCl <sub>3</sub> , CCl <sub>4</sub> , TCE, Tetrachloroethylene, Benzene	Rice bran	-	As received	F	100-600	-	-	Spherosomes (intracellular particles) involved in the adsorption; rice bran was as effective as activated carbon & superior to various other sorbents.	Adachi <i>et al.</i> 2001a
CHCl <sub>3</sub> , CH <sub>2</sub> Cl <sub>2</sub> , Trichloroethylene	Defatted seed	-	As received	-	-	-	-	Effective sorption; results were similar to those obtained with activated carbon.	Adachi <i>et al.</i> 2001b
Malathion	Bacillus cells	80C	Ground	L, F	80	-	-	Best pH 6.5; no further effect of time beyond "zero days" of equilibration	Adhikari <i>et al.</i> 2010
Trichloroethylene	Soy stover, peanut shell biochar	BC	300-700 pyrol.	L	12-32	-	-	Higher temperature yielded higher area & higher sorption capacity.	Ahmad <i>et al.</i> 2012
Trichloroethylene	Pine needles	BC	300-700 pyrol.	DR L	5-79			Higher temperature yielded higher area & higher sorption capacity; pore filling.	Ahmad <i>et al.</i> 2013

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Phenol, <i>p</i> -Nitrophenol, <i>p</i> -Chlorophenol	Activated rice husk carbon, <i>etc.</i>	AC	H <sub>3</sub> PO <sub>4</sub> , 550C	L, F, RP	8-300, 10-525, 10-500	1 <sup>st</sup>	Ex	Diffusion control with surface diffusion; external followed by internal diffusion; drops off at pH>9.	Ahmaruzzaman & Sharma 2005
Phenol, <i>p</i> -Nitrophenol	Palm fruit stones	100 C	Crushed	L, F T	115-132, 136-161	2 <sup>nd</sup>	En	Best pH=4 to 5	Ahmed & Theydan 2012
Trihalomethanes	Carbon from nut shells	AC	H <sub>3</sub> PO <sub>4</sub> , steam activate	-	-	-	-	"Enviro-filters" outperformed commercially available filters. Steam-activated carbons worked the best.	Ahmedna <i>et al.</i> 2004
Phenanthrene, Pyrene	Activated carbon	AC	Crush, sieve	-	100-200, 20-100	ID	-	Intraparticle and "branched pore" kinetic models employed.	Ahn <i>et al.</i> 2005
Benzene, Toluene, Ethylbenzene, Cumene	Rice bran	Sun	-	L	520, 690, 1000, 1100	1 <sup>st</sup>	Ex	Successful sorbent	Akhtar <i>et al.</i> 2005
2,4-Dichlorophenol	Rice husk	-	-	L	156	-	Ex	Moderate pH dependency with lowest value best; relatively low surface area	Akhtar <i>et al.</i> 2006
Benzene, Toluene, Ethylbenzene, Cumene	Horseradish pods	Sun	-	L	620, 830, 1000, 1300	1 <sup>st</sup>	Ex	Moderate pH dependency with lowest value best	Akhtar <i>et al.</i> 2007a
Methyl parathion pesticide	Rice bran, bagasse ash, sgr.cane pod, rice husk	110 C 8 h	Ground	L	114, 114, 105, 102	1 <sup>st</sup>	Ex	Regenerate by sonication with methanol.	Akhtar <i>et al.</i> 2007b
Triazophos pesticid, Methyl parathion	Chickpea husk	110 24 h	Crushed	L	2.4, 7.3	1 <sup>st</sup>	Ex	Successful sorbent	Akhtar <i>et al.</i> 2009
Phenol	Activated sludge, immob	-	-	L, F	-	-	-	pH=1, slow flow best	Aksu & Gönen 2004

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
2,4-Dichlorophenoxy acetic acid (2,4-D)	Activated carbon (gran)	AC	H-type	L	518	1 <sup>st</sup> ID	-	Best at pH=2, intraparticle diffusion rate	Aksu & Kabasakal 2003
2,4-Dichlorophenoxy acetic acid (2,4-D)	Activated carbon (powd)	AC	-	F, L	333	ID	Ex	Best at pH=2, film and intraparticle diffusion, activation energy -1.69 kJ mole <sup>-1</sup>	Aksu & Kabasakal 2005
Phenol, o-Chlorophenol, p-Chlorophenol	Dried activated sludge	60C	-	L, F	86, 102, 116	-	-	Best at pH=1, worst at pH=4	Aksu & Yener 1998
o-Chlorophenol, p-Chlorophenol	Activ. sludge, Fly ash, Gran. act. C Activ. sludge, Fly ash, Gran. act. C	60C - AC 60C - AC	- -	RP	281 99 380 287 119 422	-	-	Best at pH=1	Aksu & Yener 2001
2,4-Dichlorophenol	Activ. C from oil palm EFB	AC	Activat. in air	L	27	-	-	Best at pH=4	Alam <i>et al.</i> 2007
2-Nitrophenol	Hydrolysis lignin	-	-	L	2	2 <sup>nd</sup>	-	Chemisorption is rate-limiting; listed sorption capacity 12 dm <sup>3</sup> /g seems wrong.	Allen <i>et al.</i> 2005
Phenol	Active carbon, granulated	AC	Thermal regen.	L	126-209	-	-	Ozone thermal regeneration must be done with great care or capacity is lost.	Álvarez <i>et al.</i> 2004
Gallic acid	Active carbon, granulated	AC	Ozone regen.	L	192-287	-	-	Ozone dosage is critical it was better to oxide adsorbed gallic acid vs. directly.	Álvarez <i>et al.</i> 2009
Phenol, p-Nitrophenol, p-Chlorophenol	Active carbon, granulated	AC	-	L	140-190, 190-390, 170-350	-	-	Microporosity and pi-pi interactions were involved; surface oxygen groups catalyze oxidative coupling of phenolics.	Álvarez <i>et al.</i> 2005

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Pyrene, PCB-101	Active C from: coconut shell, anthracite. coconut shell, anthracite.	AC AC AC AC	- - - -	F	9 11 12 13	-	-	The narrower pores of the bio-based carbon were more easily clogged.	Amstaetter <i>et al.</i> 2012
Phenol, <i>p</i> -chlorophenol, <i>p</i> -nitrophenol	Activ. carbon from coir pith	AC	H <sub>3</sub> PO <sub>4</sub>	F, L	43, 63, 72	UT	-	Best pH=6; regeneration with 0.1 N NaOH	Anirudhan <i>et al.</i> 2009
Phenol, Chlorophenol, Trichlorophenol, Pentachlorophenol	Sandy aquifer media (non- viable bacteria cells)	-	-	F	2-3, 1-2, 5-15, 0.2-0.4	-	-	Lower pH favorable; adsorption was at most weakly correlated to hydrophobicity.	Antizar-L. & Galil 2004
Phenol	Green macro algae	Air	Crushed H <sub>2</sub> SO <sub>4</sub>	L	20	2 <sup>nd</sup>	-	Best pH = 6	Aravindhan <i>et al.</i> 2009
Phenol	Active carbon from seaweed	AC	ZnCl <sub>2</sub>	-	-	-	-	Best pH = 3	Aravindhan <i>et al.</i> 2011
Phenol	Dried activat. sludge	60C 24 h	-	F, L	43	2 <sup>nd</sup>	En	Best pH = 8, weak function	Arslan & Dursun 2008
Naphthalene	Aganate bead, immob. cells	-	- Ca <sup>2+</sup>	L, F, DR	18, 12	2 <sup>nd</sup>	-	Best pH > 3; Adsorbent was adversely affected by heavy metals.	Ashour <i>et al.</i> 2008
Polycyclic aromatic hydrocarbons	Active carbons	AC	-	-	-	-	-	Reduction in hydrocarbons was achieved; combined sorption & biodegradation.	Augulyte <i>et al.</i> 2008
Polycyclic aromatic hydrocarbons, <i>etc.</i>	Biologically active carbons	-	-	-	-	-	-	Semipermeable membrane was used for the separation; enzymatic action is key.	Augulyte <i>et al.</i> 2009
Petroleum components	Two active carbons	AC	-	F	400-2000	-	-	Two contacting basins in series are common.	Ayotamuno <i>et al.</i> 2006

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Phenol, Hydroquinone, <i>m</i> -Cresol, <i>p</i> -Cresol, <i>p</i> -Nitrophenol	Active carbon	AC	-	L	173, 205, 244, 208, 292	1 <sup>st</sup>	-	Best pH at “as-is” condition	Ayranci and Duman 2006
Phenol, Hydroquinone, <i>m</i> -Cresol, <i>p</i> -Cresol, <i>p</i> -Nitrophenol	Active carbon	AC	-	-	-	-	-	Best pH at “as-is” condition; Polanyi adsorption potential theory applied; adsorption was adversely affected by salinity.	Aytekkin 1991
Naphthalenic acids	Active carbon & various	AC	-	-	15	-	-	Salt sharply reduced sorption; odd dependency on sorbent amount.	Azad <i>et al.</i> 2013
Benzene (& ethanol)	Active carbon nanofibers	AC	Steam activat.	-	-	-	-	Electro-spinning of PAN; high adsorption was attributed to small diameter fibers and pi-pi interactions.	Bai <i>et al.</i> 2013
Br-dichloromethan, Benzene, Carbon tetrachloride Trichloromethane, Chloroform, Dichloromethane	Pecan shell; Pecan GAC	AC	Steam, CO <sub>2</sub> , H <sub>3</sub> PO <sub>4</sub>	-	-	-	-	The steam-activated and phosphoric acid activated pecan shell carbons achieved sorption results similar to those of commercial activated carbons, according the principle component analysis.	Bansode <i>et al.</i> 2003
Benzene, Dichlorobenzene, Phenanthrene	Grasses: rye, fescue, spinach, roots	Yes	Freeze-dried	-	-	-	-	Highest sorption was observed for the least soluble organic species; lipids in the grasses appeared to play a key role.	Barbour <i>et al.</i> 2005
Phenol, 2-Chlorophenol Phenol, 2-Chlorophenol	Fungus pellet; Dried fungus pellet	- 90C 90C	- Heated Heated	L	133 289 42 204	2 <sup>nd</sup>	-	Best pH=8; drying reduced sorption capacity.	Bayramoglu 2009



Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Lindane, Diazinon, Malathion, Pentachlorophenol, 2-Chlorobiphenyl Lindane, Diazinon, Malathion, Pentachlorophenol, 2-Chlorobiphenyl	<i>Rhizopus arrhizus</i> ;  Mixed activated sludge	Vac dr.  115 C	Auto-claved; vacuum dried  Oven dried	F	3 0.5 13 15 109 1.6 0.5 19 3 7	--		It is not clear whether the authors used high enough concentrations to exceed the adsorption capacities.	Bell & Tsezos 1987
Lindane, Pentachlorophenol, Diazinon, Malathion Lindane, Pentachlorophenol, Diazinon, Malathion	<i>Rhizopus arrhizus</i> ;  Mixed activated sludge	Vac dr.  115 C	Auto-claved; vacuum dried  Oven dried	-	-	-	-	Results were consistent with “simple adsorption”, rather than competition; bioconcentration factors were compared.	Bell & Tsezos 1988
Various solvents used in synthesis of pharmaceuticals	Activated charcoal gran.	AC	-	-	-	-	-	Pharmaceutical plant wastewater; fullerene soot was 10X more effective than activated carbon, maybe due to pi-pi interactions.	Berezkin <i>et al.</i> 2002
Gatifloxacin anti-biotic drug	Chitin	60C	.1N HCl, NaOH	L	97-182	-	En	Best pH=6	Bhowmik & Bajpai 2012
4-Chlorophenol	Commercial activated carbon	AC	-	L, T, RP	104-112	1st	Ex	-	Bilgili <i>et al.</i> 2012

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Ethylbenzene	Carbon nanotubes	-	-	-	>100	-	-	Evaluated at pH=7; the concentration of sorbate may have been too low.	Bina <i>et al.</i> 2012
Chlorohexidine; Poly-hexamethylene-biguanide	Bleached cotton	-	-	L	3-7	-	-	Electrostatic & hydrogen bonding; agglomerate of sorbate at higher concentrations	Blackburn <i>et al.</i> 2007
Catechol, Hydroquinone, Resorcinol	Activated carbons	AC	H <sub>2</sub> flow	L	178-238 169-233 163-233	-	-	Lower pH was favorable for adsorption; oxidation & reduction treatments had inconsistent effects.	Blanco-M. <i>et al.</i> 2009
Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene	Insoluble dietary fiber (barley leaves)	100 C 24 h	Amylase	-	14-37	-	-	The concentration of sorbate may have been too low.	Boki <i>et al.</i> 2007
Carbaryl, Atrazine, Parathion pesticides	Oilseed press cake	-	Optional extrac., grinding	-	1-2	-	-	Adsorption was associated with residual oils in the press-cake.; ground seeds were much less effective sorbents.	Boucher <i>et al.</i> 2007
4,4-DDT	Wood sawdust Cork waste Active carbon	110 C 24 h	Ground	L	69 19 164	2 <sup>nd</sup> ID	-	Diffusion (boundary & intraparticle) rate control; adsorption was negatively affected by organic matter in the water.	Boussahel <i>et al.</i> 2009
Naphthalene, Fluorene, Anthracene, Pyrene	Aspen wood fibers	-	As rec'd	-	-	-	-	Uptake proportional to octanol-water partition coefficients; judged to be effective for decontaminating storm runoff.	Boving & Zhang 2004
Pentachlorophenol	<i>Mycobacterium chloroph.</i>	No	Viable	F	>12	-	-	Acidic pH favors sorption; desorption at neutral pH; added amount probably below capacity of sorbent.	Brandt <i>et al.</i> 1997
Pentachlorophenol	Pine bark	105 C	Ground	L F	9	-	-	The bark had low porosity, low surface area, but high aromatic character.	Brás <i>et al.</i> 2004

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Pentachlorophenol	Pine bark	105 C	Ground	L	3	-	-	Best at low pH, no significant temperature effect was observed.	Brás <i>et al.</i> 2005
Heptachlor, Aldrin, Endrin, Dieldrin, DDD, DDT, DDE	Pine bark	105 C	Ground	-	-	-	-	A low concentration range was considered, so it was not possible to estimate adsorption capacities.	Brás <i>et al.</i> 1999
15 organic compounds	Activated carbon cloth	AC	Three types	-	-	-	-	Surface area and microporosity were found to be critical. Mesoporous carbon was more effective for larger molecules.	Brasquet & Le Cloirec 1999
Phenol	Gran. act. C, Fibrous act. C	AC	-	L	150 183	-	-	Selectivity based on the size of the micropollutant molecule.	Brasquet <i>et al.</i> 1996
Trichloroethylene, Chloroform	Active carbon	AC	-		10-60	-	-	Adsorption was correlated to Hildebrand parameters.	Browne & Cohen 1990
Fluometuron, Chloromethylpenoxy acetic acid (MCPA)	Biochars (six different types)	BC	-	-	0.05-2.0 0.05-0.3	-	-	High-area chars decreased leaching, except that soluble components gave greater leaching in some cases.	Cabrera <i>et al.</i> 2011
Benzene	Active carbon fiber cloth	AC	-	F	300-375	-	-	Mean pore size, BET surface area, and pore volume were key variables.	Cal <i>et al.</i> 1994
Phenol 2-Chlorophenol, 3-Chlorophenol, 4-Chlorophenol, 2-Nitrophenol, 2,4-Dichlorophenol, 3,4-Dichlorophenol, 3,5-Dichlorophenol, 2,4,5-trichlorophenol	Paper mill sludge	Dry	pH 8.4	LF	0.4 0.1 0.35 0.2 0.1 2 2.5 3 2.5	-	-	Particle diffusion was not the only controlling mechanism.	Calace <i>et al.</i> 2002
Phenol p-Nitrophenol	Active carbon	AC	-	-	-	-	-	Pore diffusion	Calleja <i>et al.</i> 1993

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Atrazine	Biochar from manure Active carbon	25 200, 350 -	-	-	10 18 12 117	-	-	Competition was observed between lead and atrazine for adsorption on activated carbon.	Cao <i>et al.</i> 2009
2,4-D, Paraquat	Polymerin	-	From olive mill waste water	L	14.7-40.5 137-233	-	-	Humic-like sorbents	Capasso & De Martino 2010
Phenol, 4-Nitrophenol, 2,4-Dinitrophenol, 4-Chlorophenol, 2,4-Dichlorophenol	Active carbon	AC	From olive stones	L	246 306 307 316 333	-	-	Pore size and surface acidity were important.	Caturla <i>et al.</i> 1988
Di(ethylhexyl)phthalate (DEHP)	<i>Sargassum s</i> seaweed	60C 24h	Option: bleach	-	-	-	-	Photocatalytic oxidation of the adsorbed toxin was very effective.	Chan <i>et al.</i> 2007
Phenanthrene, Fluoranthene, Pyrene	<i>Selenastrum c</i> green alga	-	-	-	-	-	-	Degradation pathway evidence	Chan <i>et al.</i> 2006
Toluene	Gran. active carbon bed	-	-	FS	163-267	-	-	Homogeneous surface diffusion limited; breakthrough curves modeled; desorption	Chatzopoulos & Varma 1995
Toluene	Gran. active carbon bed	-	-	FS	250	-	-	Homogeneous surface diffusion limited; breakthrough curves modeled; desorption	Chatzopoulos <i>et al.</i> 1994
Naphthalene, 1-Naphthol	Nine biochars from orange peel	BC	150-700 C limited oxygen	Lin F	2-30+ 20-100+	-	-	Increasing temperature caused transition from linear to Freundlich adsorption; a polar effect seems to have been important.	Chen & Chen 2009
Phenanthrene	Root tissue fractions	75C	Optional saponif.	-	>2	-	-	The suberin component was found to have high sorption capacity.	Chen & Schnoor 2009

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Naphthalene, Nitrobenzene, m-dinitrobenzene	Biochar from pine needles	100-700 C	1M HCl	-	100-450	-	-	Higher heating yielded higher sorption.	Chen <i>et al.</i> 2008
Phenanthrene, Pyrene	<i>Phanerochaete c.</i>	-	Viable mycelia	F	-	-	-	Combined biosorption & biodegradation shown.	Chen & Ding 2012
Naphthalene, Phenanthrene, Phenol, 1-Naphthol	Plant cuticles (green pepper fractions)	FD	Boil, freeze-dry, grind; Dewax	F	1-20, 1-10, 100-400, 10-200	-	-	Polarity of the solute and accessibility to surface sites were key factors; Low affinity behavior apparent.	Chen <i>et al.</i> 2005
1-Naphthol	Tomato cuticle sheet fractions	Dry	Oxalic, dewax	F	40-160	-	-	Cutin makes a key contribution to sorption; hydrophobic and H-bonding interactions.	Chen & Li 2007
Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Pyrene	White rot fungi	-, 60C 24h	Live, killed	F	-	-	-	Biosorption might restrict biodegradation; low affinity behavior.	Chen <i>et al.</i> 2010
Naphthalene, Acenaphthene, Fluorene, Phenanthrene, Pyrene	Wood chips, ryegrass roots, orange peels, bamboo leaves, pine needles	Air 25C	Ground	F	0 -1.5	-	-	Low affinity; removal of polar components by acid hydrolysis increased uptake.	Chen <i>et al.</i> 2011
Phenol	Mesoporous active carbon fr. pokeweed	AC	450, then 900C	L	172	-	-	Potassium in the pokeweed helps activate the carbon.	Chen <i>et al.</i> 2012a

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Naphthalene	Biochar series	BC	150-700	F	0.02-177	-	-	Diffusivity was the key factor; low affinity behavior evident; intermediate temp the micropores were hard to access; capacity increased with carbonation temperature.	Chen <i>et al.</i> 2012b
Naphthalene, 1,2-Dichlorobenzene	C-60 (Bucky-balls)	-	-	-	5-50	-	En	Low affinity behavior; best results when C60 was well dispersed in water.	Cheng <i>et al.</i> 2005
Phenol	Loofa vegetal cords	105	NaOH, bleach	L	5	-	En	Bleaching with peroxide increased uptake greatly.	Cherifi <i>et al.</i> 2009
p-Nitrophenol	Active carbon	AC	-	F RP	4	-	Ex	Breakthrough curves	Chern & Chien 2002
Toluene vapor	Peats (2), Compost	65C 48h	-	-	0.5-14 1-4	-	-	Pore filling mechanism	Chiu <i>et al.</i> 2003
1,2,3,4-Tetrachlor. Dibenzofuran, PCDD/Fs, PCBs Chlorobenzenes, Chloronaphthalenes	<i>Bacillus pumil.</i> exudates	-	Boiled to release chems.	-	-	-	-	Uptake amounts are expressed based on volume of sorbent, not mass; hard to compare; proteins sorbed much more than the carbohydrates or the insulin.	Choi <i>et al.</i> 2003
1-Methylcyclopropene	Fruit & veg. tissues	No, Yes	- 50C	-	-	-	-	External tissues had greater sorption; drying reduced sorption; pectins & lignin were sinks for sorption; rates compared.	Choi & Huber. 2009
Benzene	Active carbon bed	AC	-	-	650	-	Ex	Simulation based on kinetic model.	Chuang <i>et al.</i> 2003a
Benzene vapor	Active carbon bed	AC	-	L	200-450	-	Ex	Simulation based on kinetic model.	Chuang <i>et al.</i> 2003a
Perfluorooctane sulfonate	Granulated active carbon	AC	-	F	455	-	-	Regeneration highly successful with methanol solutions of NaOH, NaCl.	Chularueang-aksorn 2013

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Phenanthrene	<i>Sargassum hemiphyllum</i>	50C 16h	-	-	0.4-0.5	2 <sup>nd</sup>	En	Shaking sped up sorption.	Chung <i>et al.</i> 2007
Benzene Toluene Ethylbenzene m,p-Xylenes o-Xylene	Angico sawdust & peat	Air 25C	None	L	0.002 to 0.011 reported for whole set	-	-	Peat performed better than the sawdust.	Costa <i>et al.</i> 2012
Phenol, Nitrobenzene	Carbon	BC	Acidity content	-	10-100 50-200	-	-	Oxygen content of carbon suppressed adsorption.	Coughlin & Ezra 1968
Phenol, Nitrobenzene, Na benzenesulfon.	Carbon	BC	-	-	10-100 50-200 -	-	-	Dilute phenol adsorption was reduced by oxygenated sites.	Coughlin <i>et al.</i> 1968
Naphthalene, Acenaphthene, Anthrene Pyrene	Bagasse, Green cocon., Chitosan, Chitin	Dry	-	F	0.1-0.8	-	-	Lignin seemed to be mainly responsible for adsorption.	Crisafulli <i>et al.</i> 2008
p-Nitrophenol	Active carbon fr. cedar wood	AC	H <sub>2</sub> SO <sub>4</sub> & CO <sub>2</sub>	L	300-630	-	-	Surface sulfur appeared to inhibit uptake of p-nitrophenol; previous dehydration favored activation & adsorption.	CuerdaCorrea <i>et al.</i> 2006
Chloroform, DiChlormethane, Bromoform	Humin from peat bog	Air 25C	Ground	-	18-21	2 <sup>nd</sup>	-	Humin was found to be effective.	Cunha <i>et al.</i> 2010
Phenol, Cresols, Nitrophenols, Chlorophenols	Active carbon	AC	H <sub>3</sub> PO <sub>4</sub>	L	232-339	-	-	Uptake was inversely proportional to solubility and pK <sub>a</sub> ; uptake also correlated to molecular size; they did not measure pH or temperature.	Daifullah & Girgis 1998

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
BTEX: Benzene, Toluene, Ethylbenzene, Xylene	Active carbon fr. date pits, cotton stalk, peach stones, almond shell, olive stone	AC	H <sub>3</sub> PO <sub>4</sub> post-tr., 773K	-	1-9 4-9 5-9 5-10	-	-	B < T < E < X uptake consistent with decreasing solubility and increasing molecular weight; air oxidation gave higher uptake per unit area.	Daifullah & Girgis 2003
Quinalphos, Lindane pesticides	Bio-activated carbon	-	Danube River flora	-	-	-	-	Adsorption & microbiological degradation happen simultaneously; the system worked better for the quinalphos; flow-through.	Dalmacija <i>et al.</i> 1992
Phenol and its successively coupled multimers	Active carbon	AC	-	L	20-90	-	-	Adsorption capacity increased with the size of the molecule.	Dargaville <i>et al.</i> 1996
p-Cresol	Biochar from pine	BC	K <sub>2</sub> CO <sub>3</sub> 300-400	L	5-7	-	Ex	Adsorption inhibited by acidic groups.	Das <i>et al.</i> 2013
2,4,6-Trichlorophenol	<i>Bacillus subtilis</i>	No	Live culture	-	-	-	-	Best pH<5; stability constant fits	Daughney Fein 1998
Phenol, 2-Chlorophenol, 2,6-Dichlorophenol	<i>Daucus carota</i> <i>Ipomoea bat.</i> <i>Solanum avi.</i>	No	Cultured	-	-	-	-	Roots were effective in removing phenols.	De Araujo <i>et al.</i> 2006
2,4-Dichlorophenol & other contaminants	Horseradish, Potato, White radish	No	- - H <sub>2</sub> O <sub>2</sub>	-	-	-	-	Showed effective biodegradation with peroxidases; in the absence of H <sub>2</sub> O <sub>2</sub> the removal was much less effective.	Dec & Bolag 1994
2,4-Dichlorophenol	<i>Posidonia oceanica</i> L.	60C 48h	-	L, F	5-13	2 <sup>nd</sup>	-	Seagrass; best pH 3 to 7;	Demirak <i>et al.</i> 2011
Phenol, o-Chlorophenol, p-Chlorophenol, 2,4,6-Trichlorophen.	Phanerochaet chrysosporium	30C 24h	Ground	(L)	113 193 225 424	-	-	Methanol was used for regeneration of the fungus.	Denizli <i>et al.</i> 2004



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Phenol, o-Chlorophenol, p-Chlorophenol, 2,4,6-Trichlorophen.	<i>Pleurotus sajor caju</i>	30C 24h	Ground	(L)	89 159 189 373	-	-	Higher pH gave higher uptake on the fungus.	Denizli <i>et al.</i> 2005
PCB in soil	Biochar	BC	-	-	-	-	-	Biochar reduced PDB uptake by plants.	Denyes <i>et al.</i> 2012
Pentachlorophenol	Active carbon	AC	-	-	260-500	-	Ex	Adsorption decreased with increasing pH; pi-pi interactions on basic sites cited.	Diaz-Flores <i>et al.</i> 2006
Phenanthrene, Pyrene	<i>Phanerochaet chrysosporium</i>	-	Live, Heat-killed	-	-	-	-	Both biosorption & biodegradation were shown to be important; live material showed an advantage for removal.	Ding <i>et al.</i> 2013
Befenthrin	Cork (granulated)	105 C	-	L	0.26-0.55	-	-	The low uptake is consistent with the impervious nature of cork.	Domingues <i>et al.</i> 2005
Ci-cypermethrin	Cork, Active carbon	105 C	-	L	0.3 0.2	-	-	States that cork is successful; however the reported numbers were very low.	Domingues <i>et al.</i> 2007
4-Chlorophenol, 3,5-Dichlorophenol, 2,4,6-trichlorophen., 2,3,4,6-tetrachlorop, Pentachlorophenol	Carbon black	BC	-	L	296 277 237 230 239	-	Ex	Best pH<11	Domínguez-V. <i>et al.</i> 2009
Phenol	<i>Spirulina bionanopart.</i>	60C	Ground	L	159	-	Ex	Best pH=6; very strong temperature effect	Dotto <i>et al.</i> 2013
Phenol	Carbonized beet pulp	BC	600C	F, L	70-90	2 <sup>nd</sup>	En	Best pH=6	Dursun <i>et al.</i> 2005
Phenol, Pentachlorophenol	Carbonized pine bark	BC	672C	L, F	18-40 1	-	-	Slow carbonization	Edgehill & Lu 1998

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Aldrin, Dieldrin, Endrin pesticides	Date stones	300 C	-	F	16 14 12	2 <sup>nd</sup>	Ex	Thermal treatment increased the sorption capacity.	El Bakouri <i>et al.</i> 2009
Chlorophenols, Nitrophenols	Torrefied olive wood	100-300	Wash	-	(40-90% recov.)	-	-	Heating and washing may have made pores more accessible. Weak pH effect.	El-Sheikh <i>et al.</i> 2011
Phenol, 2-Chlorophenol, 3-Chlorophenol, 4-Chlorophenol, 2-Nitrophenol, 4-Nitrophenol, 2,4-Dinitrophenol	Olive wood	-	Ground	L, F	8, 12, 12, 12, 6, 10, 6	2 <sup>nd</sup>	-	Adsorption improved by solvent washing; pore diffusion.	El-Sheikh <i>et al.</i> 2013
Pentachlorophenol	Almond shell	30C opt.	Ground	F, lin	0.3	-	-	Very low affinity, especially at low concentration; "good natural adsorbent"	Estevinho <i>et al.</i> 2006
Benzopyrene, PAHs	Biochars	VC	Various	-	0.00001-0.0007	-	-	Soxhlet extraction with acetone/ cyclohexane mixture effective to remove trace amounts already present in biochars.	Fabbri <i>et al.</i> 2013
Phenol	<i>Phanerochaet chrysosporium</i>	Not	Immobil., free	L	3-14	2 <sup>nd</sup>	-	Best pH=5.5	Farkas <i>et al.</i> 2013
o-Chlorophenol, m-Chlorophenol	Active carbons fr. olive stones	AC	1113 K	-	320 313	-	-	Various solvents were used to regenerate carbons; heating causes chemisorption.	Ferro-Garcia <i>et al.</i> 1996
Phenol	Active carbons	AC	NaOH, KOH	L	213-238	2 <sup>nd</sup>		Carbon from kraft lignin performed the best.	Fierro <i>et al.</i> 2008
Nitrobenzene, Benzoic acid, " "	Active carbon	AC	- pH=11.5 pH=3	L	290-360 11-22 200-220	-	-	Oxygen groups lowered sorption from cyclohexane solution; high pH suppressed benzoic acid sorption on all carbons.	Franz 2000
Phenol. p-Nitrophenol	Active carbon	AC	-	-	280 560	-	-	Competition between the two phenols was observed and accounted for.	Fritz & Schlunder 1974

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TNT red water	Charcoal from bamboo	AC	-	L	23-29	2 <sup>nd</sup> ID	En	Intraparticle diffusion affects rate. Sorption affected by charge, H bonding, acid-base.	Fu <i>et al.</i> 2012a
TNT red water	Active carbon from rice husk	AC	SiO <sub>2</sub> remov.	-	3-8	2 <sup>nd</sup>	-	Effective low-cost adsorbent	Fu <i>et al.</i> 2012b
Phenol, p-Chlorophenol, o-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophen, p-Nitrophenol, 2,4-Dinitrophenol, 2,4,6-Trinitrophenol	Active carbon (granular)	AC	-	F	100-500 130-600 130-600 160-800 200-1000 140-560 100-150 100-230	-	-	Interpretation based on percentage of surface coverage of the carbon; the result was interpreted using molecular orbital theory and molecular size.	Furuya <i>et al.</i> 1997
Phenols in olive mill wastewater	Active carbon fr. olive stones	AC	Steam 850,800	L	6-90	1 <sup>st</sup>	-	Mesoporosity is key; those carbons with best-developed mesopores exhibited the highest uptake.	Galiatsatou <i>et al.</i> 2002
Nonylphenol	<i>Chorella</i> sp. (4 species)	No	Living; 121C	-	0.4-18	-	-	Biodegradation rate was affected by light and temperature; but removal from water was the same with live or dead cells.	Gao <i>et al.</i> 2011
4-Chlorophenol, 2,4-Dichlorophenol	Anaerobic gran. sludge	No	Fresh (refrig.)	L, F	1.5 5	-	En	Low pH best.	Gao <i>et al.</i> 2007
Gallic acid, p-Hydroxybenzoic, Syringic acid	Active carbon	AC	-	-	250 220 200	-	En	Competition effects at high concentration.	García-Araya <i>et al.</i> 2003
Lindane pesticide	<i>Rhizopus oryzae</i>	No	Dead, autocl.	F, L	0.1	2 <sup>nd</sup>	-	Sorption was independent of pH & temperature; high affinity but low capacity.	Ghosh <i>et al.</i> 2009
Phenanthrene	Carbon single wall nanotube	-	-	-	70-300	-	-	From ethanol solution; purification of the carbon improved phenanthrene uptake.	Gotovac <i>et al.</i> 2006

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Naphthalene	Carbon single wall nanotube	-	-	-	-	-	-	From trichloroethylene solution; the sorbate was on the outer surfaces.	Gotovac <i>et al.</i> 2007a
Phenanthrene, Tetracene	Carbon single wall nanotube	-	-	-	50-350 100-600	-	-	From toluene solution; acid functionalization increased sorption markedly.	Gotovac <i>et al.</i> 2007b
Phenol	Active carbons	AC	-	-	30-38	-	-	Regeneration by acetone leaching; differences in surface groups did not account for irreversible sorption; lower pH favors irreversible adsorption.	Grant <i>et al.</i> 1990
DDD, DDE	Fly ash from bagasse	FA	H <sub>2</sub> O <sub>2</sub>	L, F	0.008 0.007	-	Ex	Best pH=6; high removal percentages	Gupta & Ali 2001
Endosulfan, Methoxychlor	Active carbon	AC	450C HCl	L, F	34 36	2 <sup>nd</sup>	Ex	Best pH low, <8	Gupta & Ali 2008
Methoxychlor, Methyl parathion, Atrazine	Active carbon from rubber	AC	KOH 900C	L	112 89 105	1 <sup>st</sup>	Ex	Pore sorption control	Gupta <i>et al.</i> 2011
Phenol, p-Nitrophenol	Fly ash from bagasse	FA	H <sub>2</sub> O <sub>2</sub>	L, F	0.5-0.7 0.7-1.2	-	Ex	Best pH<8	Gupta <i>et al.</i> 1998
2,4,6-Trinitrophenol, 4-Nitrophenol, 4-Chlorophenol, 1,3-Dihydroxybenzn	Carbon from fertilizer waste	BC	450C HCl	-	98-130 77-104 62-99 50-92	-	-	Column tests gave higher capacities than the corresponding batch tests.	Gupta <i>et al.</i> 2000
Benzoic acid, p-Nitrophenol, p-Cresol, Salicylic acid, Nitrobenzene	Activated carbons (commercial)	AC	-	-	180-187 207-238 166-175 199-200 229-244	-	-	Adsorption depended on molecular size; sideways (T-shaped) orientation in the pi-stacking of aromatic adsorbates.	Haghseresht <i>et al.</i> 2002a

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Benzoic acid, p-Nitrophenol, p-Cresol, Salicylic acid, Nitrobenzene	Activated carbons (commercial)	AC	-	-	180-234 207-239 166-221 199-293 229-266			Adsorption of dissociable aromatic compounds provides evidence of London dispersion contribution to adsorption.	Haghseresht <i>et al.</i> 2002b
Benzoic acid, p-Nitrophenol, p-Cresol, Salicylic acid, Nitrobenzene	Activated carbons (commercial)	AC	-	-	186 236 176 193 246	-	-	Adsorption falls above critical pH value: Benzoic & salicylic acids: pH ~6; p-Nitrophenol & cresol: pH ~10.	Haghseresht <i>et al.</i> 2002c
p-Nitrophenol, p-Cresol, Nitrobenzene	Activated carbons (commercial)	AC	-	-	153-208, 119-151, 154-209	-	-	Binary isotherms predicted; oxidation reduces capacity moderately (15-20%).	Haghseresht <i>et al.</i> 2003
Phenol	Activated charcoal	AC	-	F, L, RP	48	-	Ex	Large drop in adsorption about pH 10; scant effect of salt	Halhouli <i>et al.</i> 1995
Paraquat dichloride	Activated carbon	AC	CO <sub>2</sub> 900C	L	28-34	2 <sup>nd</sup>	Ex	Particle size did not make a clear difference; regenerate at high pH.	Hamadi <i>et al.</i> 2004
Phenol, 2-Chlorophenol, 4-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophen.	Granular activated carbon	AC	-	FG HB T F	238-250, 284-303, 356-301, 303-370, 438-482	-	-	No association among the adsorbed molecules detected; capacity increased with molecular weight, hydrophobicity, decreased solubility; various forms of Langmuir model gave similar results.	Hamdaoui & N. 2007a
4-Chlorophenol	Activ. carbon from rattan sawdust	AC	-	L	189	2 <sup>nd</sup>	-	Intra-particle diffusion; gradual dropoff in capacity above pH=7	Hameed <i>et al.</i> 2008a

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Phenol	Activ. carbon from rattan sawdust	AC	KOH, 850C	L	149	2 <sup>nd</sup>	-	Dropoff in capacity above pH=8	Hameed <i>et al.</i> 2008b
2,4,6-trichlorophenol	Activated carbon	AC	KOH, 814C	L	169	-	-	Activation conditions were optimized.	Hameed <i>et al.</i> 2009
p-Nitrophenol	Magnetic activated carbon	AC	-	L	128-133, 61-72	-	-	Coprecipitation was effective for magnetizing the carbon.	Han <i>et al.</i> 2013
Phenol	<i>Pseudomon.</i> on active C	-	-	-	-	-	-	Adsorption happens first, then biodegradation; packed bed.	Hank <i>et al.</i> 2010
Perfluoroacetic acid & related compounds	Gran & powd. activated carbon	AC	-	L, F	0.05-50	-	-	Some of the surfactants exhibited tiny values of adsorption capacity; low bulk concentrations were employed.	Hansen <i>et al.</i> 2010
Atrazine	Biochars from corncob	BC	350-650C	F	0.5-3	-	-	The capacity Increased with higher temperature of charring; low affinity.	Hao <i>et al.</i> 2013
p-Nitrophenol	Activated carbons	AC	HNO <sub>3</sub> NaOH	-	300-500	-	-	Oxidation decreased the surface area but had little effect on adsorption.	Haydar <i>et al.</i> 2003
Phenol	Activated carbons	AC	CO <sub>2</sub> 900C	-	60-200	-	-	Different adsorption energies on different sizes of pores; pore-filling mechanism.	Hsieh & Teng 2000
Paraquat	Rice husk	50C	Methacrylic acid	L	292	-	-	The carboxylate form (NaOH) was effective for paraquat removal.	Hsu <i>et al.</i> 2009
Paraquat	Rice husk	50C	Methacrylic acid	L	318	-	-	-	Hsu & Pan 2007
Methyltertbutyl ether MTBE	Biolog. active. carbon	-	-	-	1-20	-	-	Bioaugmentation was used to regenerate the carbon adsorbent <i>in-situ</i> , adsorption was mainly on the bacterial surfaces.	Hu <i>et al.</i> 2013

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
1-Naphthylamine	Multiwall carbon nanotubes	-	-	L	154-294	2 <sup>nd</sup>	En	Best pH range 7-9; pi-pi interactions; magnetic particles were effective for remediation with separation.	Hu <i>et al.</i> 2011
Phenanthrene; Pyrene	Aspen wood fibers	-	Bleach, Hydrol.	F	0.01-5.0 0.01-10	-	-	Bleaching decreased uptake; hydrolysis of carbohydrates increased uptake.	Huang <i>et al.</i> 2006
Anthracene	<i>Gomphidius viscidus</i>	No	Auto-claved	L	1500-1900	2 <sup>nd</sup>	-	Fungal biomass most effective at pH>6; fungus could become acclimated.	Huang <i>et al.</i> 2010
Phenol, 3-Nitrophenol	Activated carbons	AC	Up to 1000C	-	10-20, 10-20	2 <sup>nd</sup> ID	-	Intraparticle diffusion	Ioannou & Simitzis 2009
Phenol	Bio-active carbon	-	Commercial	-	-	-	-	Substituted phenols inhibited the biofilm; packed bed system; >90% biodegradation in 20-30 days	Ivancev-T. <i>et al.</i> 1998
Pentachlorophenol	Microbial biomass	No	-	-	-	-	-	Higher uptake onto activated sludge at lower pH	Jacobsen <i>et al.</i> 1996
Phenol, 2-Chlorophenol, 4-Chlorophenol, 2,4-Dichlorophenol	Carbon slurry, <i>etc.</i>	BC	500C	L	17, 50, 57, 132	1 <sup>st</sup>	-	Pore diffusion	Jain <i>et al.</i> 2004
Phenanthrene	Biochars from wood	BC	300 to 820C	F	2-30	-	-	Low-affinity isotherms; heating at above 450 °C greatly increased uptake.	James <i>et al.</i> 2005
Tetracycline	Carbon nanotubes	-	-	F		-	-	Humic acids suppressed adsorption of tetracycline; Cu(II) increased adsorption.	Ji <i>et al.</i> 2010

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Phenanthrene, Anthracene, Fluoranthrene, Benz[a]anthracene, Benzo[fluoranthene, Benzo[g,h,i]perylene	Diesel soot from car exhaust pipes, other soots	-	-	-	-	-	-	Adsorption of the aromatic compounds onto soot was very strong and largely irreversible, according to isotopic tests; preferential adsorption of planar molecules.	Jonker & Koelmans 2002
Lindane	Gram – bacter Gram + bacter	Not, 100	Live or dired	F	0.1-1	-	-	Zeta potential was correlated with adsorption; Van der Waals interactions.	Ju <i>et al.</i> 1997
Phenol, 4-Chlorophenol	Active carbon	750-840	Steam active.	L	240-300; 250-400	-	En	Adsorption in micropores seems likely.	Juang <i>et al.</i> 2001
Phenol, 4-Chlorophenol, 4-Nitrophenol	Active carbon fibers	AC	-	L	110-140, 240-260, 230-240	-	-	Jossens <i>et al.</i> 3-parameter heterogeneous thermodynamic isotherm fit best; rate data fit two-phase model.	Juang <i>et al.</i> 1996a
Phenol, Chlorophenols, Cresols	Active carbon fibers	800-1200	-	-	150, 240-264, 199-209	-	-	Higher adsorption of chlorinated, compared to methylated phenols	Juang <i>et al.</i> 1996b
Phenols	Active carbon, plum kernel	750-900	Steam activat.	L	106-258	2 <sup>nd</sup> ID	-	Intraparticle diffusion, hydrogen bonding	Juang <i>et al.</i> 2000
DDT, DDD, DDE	Fungal mycelia	-	-	-	-	-	-	Dichloromethane was used to extract the chlorinated pesticides from the fungal mycelia.	Juhasz & Naidu 2000b
<i>p,p'</i> -DDT	<i>Cladosporium</i> fungal mycel.	no	-	-	7-17	-	-	Killed biomass adsorbed somewhat more than living; little effect of pH.	Juhasz <i>et al.</i> 2002
Phenol, Chlorophenols	Granular act. carbons	AC	-	F	0.5-10	-	-	Starting bulk concentrations were too low; dispersion forces proposed important.	Jung <i>et al.</i> 2001



Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
2-Chlorophenol, 2,4-Dichlorophenol	Fly ash from power plant	FA	-	F	1.3 2	-	Ex	Carbon content and specific surface area were correlated with uptake; packed bed; lower adsorption above pH=7.	Kao <i>et al.</i> 2000
Phenol	Hydrogel-biochar composites	BC	-	L	14-23	1 <sup>st</sup>	-	Increasing salt increased uptake	Karakoyun <i>et al.</i> 2011
Trichloroethylene	Active carbons	AC	-	F	1-100	-	-	Many different activated carbons were compared; 5 nm pore volume is key.	Karanfil & Dastgheib 2004
Trichloroethylene	Active carbon fibers	AC	-	F	1-100	-	-	Natural organic matter can be excluded with a membrane.	Karanfil <i>et al.</i> 2006
2-Nitrophenol	Active carbons	AC	-	-	500-550	-	-	Most of the adsorbed phenol did not come off when bulk concentration was lowered.	Karimi-J. & N. 1997
Chlorophenols	Anaerobic gran. sludge	No.	Live sludge	F	0.1-2	-	-	Linear adsorption isotherms were weakly correlated to octanol-water partition coefficients.	Kennedy <i>et al.</i> 1992
Phenol	Mesoporous carbon	700-900	-	F, L	22	2 <sup>nd</sup>	Ex	Highest adsorption at low pH.	Kennedy <i>et al.</i> 2007
Nefenamic acid pharmaceutical	Active carbon	AC	-	L	100	-	-	Activated carbon outperformed membrane ultrafiltration.	Khalaf <i>et al.</i> 2013
Phenol, <i>o</i> -Chlorophenol, <i>m</i> -Chlorophenol, <i>p</i> -Chlorophenol, <i>m</i> -Cresol	Active carbon	AC	-	F, L	160-220	-	-	Larger molecules of lower solubility in water adsorb to a greater degree.	Khan <i>et al.</i> 1997a

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Toluene, Acetone, <i>p</i> -Cresol, <i>p</i> -Chlorophenol, Benzene, <i>n</i> -Pentanol, 4 <i>n</i> -Propylphenol, <i>p</i> -Methylphenol	Active carbon	AC	-	L	260, 50, 19, 260, 200, 43, 200, 95	-	-		Khan <i>et al.</i> 1997b
Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene	Cat-tail fibers; Kapok fibers	60C 24h	Cat-tail was ground	F	0.05-0.6	-	-	Cat-tail fibers were more effective than kapok fibers; low affinity isotherms.	Khan <i>et al.</i> 2007
Dichloromethane	Commercial G active carbon	AC	-	F L	46	2 <sup>nd</sup> 1 <sup>st</sup>	Ex	Best pH 6-8; different carbons showed different fits.	Khan <i>et al.</i> 2010
16 multi-ringed compounds	Biochar from sewage. sludge	BC	500C	-	-	-	-	The biochar reduced bioaccumulation of polyaromatic hydrocarbons by lettuce.	Khan <i>et al.</i> 2013
2,4-Dichlorophen-oxyacetic acid	Magnetic & graphitic C	BC	Fe <sub>3</sub> O <sub>4</sub> $\mu$ -wave	L	33-77	2 <sup>nd</sup>	-	The magnetic powders are easily separated.	Khoshnood & A. 2012
Trichloroethylene	Granular active carbon	AC	-	F	1-80	-	-	Preloaded with humic substances; effects of calcium and salt; low affinity	Kilduff <i>et al.</i> 1998
Phenol	Active carbon from tobacco residues	AC	K <sub>2</sub> CO <sub>3</sub> , KOH 700C	L	18, 46	2 <sup>nd</sup>	-	-	Kilic <i>et al.</i> 2011

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Phenol	Powder act. C, Alginate bead, Alginate C mix	AC	As-received	L	113 3 75	-	-	Ideal adsorbed solution theory was used to predict the adsorption on beads formed from alginate and activated carbon.	Kim <i>et al.</i> 2011
Dibromochloro-propane; Trichloroethylene	Active carbons from almond shells	AC	850C steam	-	100-115	-	-	Nut source did not influence the results.	Klasson <i>et al.</i> 2010
Trichloroethylene	Active carbons from flax & cotton	AC	H <sub>3</sub> PO <sub>4</sub> ; Steam	L	64-80	-	-	Also evaluated adsorption from the gaseous phase.	Klasson <i>et al.</i> 2009
Phenanthrene, Naphthalene, Acenaphthene	Active carbon from soybean stalk	AC	H <sub>3</sub> PO <sub>4</sub> 700C	-	-	-	-	Uptake increased with carbonation temperature and carbon content.	Kong <i>et al.</i> 2011a
Phenanthrene	Biochar from soy stalk	BC	300-700C	F	7-30	-	-	Linear & Toth adsorption isotherms; found competition with Hg(II) adsorption.	Kong <i>et al.</i> 2011b
Phenanthrene	Active carbon, sesame stalk	AC	H <sub>3</sub> PO <sub>4</sub> 700C	LF	10-16	-	-	Hydrophobic interactions	Kong <i>et al.</i> 2012
N-nitrosodiethylamine, N-methyl-N'-nitro-N-nitrosoguanidine	Lignin preparations	-	-	-	-	-	-	Genotoxics bind to lignin but not to polysaccharides.	Košíková <i>et al.</i> 2009
p-Chlorophenol	Active carbon apricot stone	AC	-	-	20-55	ID	-	Intraparticle diffusion in three phases, was shown by square-root time dependency.	Koumanova <i>et al.</i> 2003
Phenol	Polymeric resins	-	-	-	-	-	-	Membranes all were selective for phenol in mixtures with acetone; NaOH regeneration.	Kujawski <i>et al.</i> 2004
Dibenzothiophenes (from kerosene)	Active carbon from rice husk	AC	850C in CO <sub>2</sub>		0.05-0.06	-	-	Pore size distribution was the key factor	Kumagai <i>et al.</i> 2009

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Phenol, 4-Nitrophenol	Granular active carbon	AC	-	RP F	166; 206	ID	-	Intraparticle diffusion with three phases	Kumar <i>et al.</i> 2007
Estriol endocrine disrupter	Activated charcoal	-	-	L	0.003	1 <sup>st</sup>	Ex	Film diffusion control of rate	Kumar <i>et al.</i> 2009a
Acrylonitrile	Fly ash from bagasse	FA	Sugar mill		18-91	-	-	Two-step Langmuir adsorption	Kumar <i>et al.</i> 2008
Phenol, 2-Chlorophenol, 4-Chlorophenol	<i>Trametes versicolor</i>	70C	Crushed	L	50; 86; 112	1 <sup>st</sup>	-	NaOH was used for regeneration; also the authors did packed bed tests.	Kumar <i>et al.</i> 2009b
Phenol, 2-Chlorophenol, 4-Chlorophenol	<i>Acacia l.</i> bark powder	80C	0.1N NaOH, acid	L	94, 147, 182	1 <sup>st</sup>	-	Greatest uptake at pH=7, and drop-off at higher levels	Kumar & Min 2011a
Phenol, 2-Chlorophenol, 4-Chlorophenol	<i>Schizophyllum commune</i> fungus	60C	Non-living	L	120, 178, 244	2 <sup>nd</sup>	-	Highest uptake at pH 4 to 7; regenerate with NaOH.	Kumar & Min 2011b
2,4,6-Trichlorophenol	<i>Acacia l.</i> bark powder	80C	0.1N NaOH, acid	L, E	256	2 <sup>nd</sup>	-	Highest sorption at pH=5; Langmuir and Elovich isotherm best fits.	Kumar <i>et al.</i> 2012
4-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophen.	Peat	-	-	F	-	2 <sup>nd</sup>	-	Increasing sorption in the order: 4-Chlorophenol < 2,4-Dichlorophenol < 2,4,6-Trichlorophenol	Kusmieriek <i>et al.</i> 2013
Nonylphenol	<i>Rhizopus arrhizus</i> in chitosan bead	-	Auto-claved 125C	FS RP	54-74	1 <sup>st</sup>	-	Shrinking core model; autoclaving increased uptake; regeneration using methanol	Lang <i>et al.</i> 2009
Phenol, 2,3,4-Trichlorophen.	Activated carbons	AC	-	LF	95-280 130-680	-	-	Heterogeneity was quantified using the Langmuir-Freundlich model.	László <i>et al.</i> 2003
Phenol	Activated carbons	AC	Nitric ac 900C	LF	266-279	-	-	Steam activation, Dubinin-Astakhov model used to model heterogeneous adsorption	László <i>et al.</i> 2006

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Phenol, 2,3,4-Trichlorophen.	Activated carbons	AC	Steam 900C	L	95-280 130-680	-	-	Trichlorophenol adsorption was hindered at high pH due to its lower pK <sub>a</sub> .	László & Szucs 2001
Phenol, Aniline, Nitrobenzene, Benzoic acid	Active carbon with different O content	AC	350C oxygen	F	100-210 - 278-367 30-200	-	-	Much higher adsorption at pH 3 than 11	Leng & Pinto 1997
Pentachlorophenol	Granular active carbon	AC	-	PR	200-340	ID	-	Prausnitz-Radke isotherm model; intraparticle diffusion	Leyva-Ramos <i>et al.</i> 2009a
Pentachlorophenol	Active carbon fibers	AC	-	L	230-280	ID	-	Hindered diffusion into pores	Leyva-Ramos <i>et al.</i> 2007
Naphthalene-sulphonic acid	Active carbon	AC	Ozonization	PR	70-90	ID	-	Prausnitz-Radke isotherm model; excessive ozonation greatly decreases uptake.	Leyva-Ramos <i>et al.</i> 2009b
Methyltertbutyl ether (MTBE for gasoline)	Biologically active carbon	AC	Cultured (inocul.)	F	2-40	-	-	Low affinity isotherms; microbial action gradually breaks down MTBE.	Li <i>et al.</i> 2013c
Porphyrin with long alkyl tails	Single-wall C nanotubes	-	-	-	-	-	-	Selectivity was demonstrated, leading to semi-conductivity.	Li <i>et al.</i> 2004
2,4-D; Acetochlor	Biochars	BC	200, 350, 500C	-	4-25; 4-20	-	-	Biochar added to soil slowed the release of the herbicides; low affinity isotherms.	Li <i>et al.</i> 2013a
Tetracycline	Anaerobic gran. sludge	No	Live (wet)	L	3-5	-	En	Highest adsorption was at pH=3.	Li <i>et al.</i> 2013b
<i>p</i> -Nitroalinine	Active carbon from corn stalk	AC	Phosphate	RP L	313-406	2 <sup>nd</sup>	-	Best pH 5-7	Li <i>et al.</i> 2009
MTBE; Trichloroethylene	Active carbon	AC	Three O levels	F	0.3-8; 4-50	-	-	Uptake highly dependent on micropores; uptake inhibited by natural organics; TCE adsorption falls with incr. O + N content	Li <i>et al.</i> 2002

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Phenanthrene	Fruit cuticles; Potato perid.	60C	fractions	F	1-7	-	-	Cutin and suberin components played big role in adsorption; low affinity	Li & Chen 2009
Phenanthrene; Pyrene	Pine bark	60C	Extract, Saponif, Hydrol, etc.	-	0-6	-	-	Lignin had the largest contribution to adsorption; bulk concentrations too low; low affinity isotherms; acid hydrolysis had good effect by removing polysaccharides.	Li <i>et al.</i> 2010a
4-Chlorophenol, 2,4-Dichlorophenol, 2,4,6-Trichlorophen.	Fruit cuticles; Potato perid.	60C	fractions	F	0-100	-	-	Cutin and suberin components played big role in adsorption; low affinity.	Li <i>et al.</i> 2012
Phenanthrene	Tea leaf powder	70C	Brewed	F	0-5	-	-	Low affinity; aliphatic carbons in tea leaves correlated with uptake.	Lin <i>et al.</i> 2007
Organic carbon	Biochars	BC	-	-	0.004-0.8	-	-	Hot water extraction of organics already present in various biochars	Lin <i>et al.</i> 2012
Phenol; Aniline	Active carbon	AC	-	L	200-300, 200-300	-	-	Poor fits to Langmuir model actually; the ideal adsorbed phase model was used.	Liu & Pinto 1997
Pentachlorophenol	Biochar from rice straw	BC	Open burning	F	30-45	-	-	The biochar benefited germination and plant growth <i>in-situ</i> .	Lou <i>et al.</i> 2011
Trihalomethanes	Carbon nanotubes	-	-	L	1-2.5	-	-	Capacity drops off above pH=7.	Lu <i>et al.</i> 2005
Trihalomethanes	M.-W. carbon nanotubes	-	-	L	0.3-3	1 <sup>st</sup>	Ex	Proposed for drinking water treatment.	Lu <i>et al.</i> 2006
Benzene; Toluene; o-Xylene	Wood chips: fir & pine	-	Water-soaked	Lin	0-6	-	-	Fractional lignin content of wood correlated with the adsorption capacity.	Mackay & G. 2000
Phenol	Active carbon	AC	Oxidation	L	16-20	-	-	Oxidation adversely affected phenol adsorption.	Mahajan <i>et al.</i> 1980
Phenol	Rice husk; Rice husk ash	100 -	- 400C	F L	0.002 0.89	1 <sup>st</sup>	-	Ashing greatly increased adsorption.	Mahvi <i>et al.</i> 2004

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Toluene	Carbon aerogels	AC	900C steam	-	1360	-	-	Initial carbonation was at 500 or 1000C; regenerated at 400C.	Maldonado-H. <i>et al.</i> 2007
Atrazine pesticide	Active C fiber Gran. act. C	AC	800-1000C	-	-	-	-	Column tests (breakthrough); wide-open microstructure of carbon highly beneficial.	Martin-G. & Font 2001
Pentachlorophenol	<i>Aspergillus niger</i> fungi	60C	- various	F	3-10	2 <sup>nd</sup>	Ex	Decreased uptake with increasing pH, except if adsorbent was cationized	Mathialagan & V. 2009
Phenol, <i>p</i> -Nitrophenol, Nitrobenzene	Activated carbon	AC	-	-	150-260 235-280 230-290	-	-	Acid-base interactions proposed	Mattson <i>et al.</i> 1969
Phenol, Resorcinol, 2-Chlorophenol	Rice husk ash	FA	Muffle furnace	L F	15, 8, 0.2	-	-	Maximum adsorption near neutral pH.	Mbui <i>et al.</i> 2002
Carbofuran; Methyl parathion	Chestnut shells	110 C	Nitric acid	L	2.4, 6	ID 1 <sup>st</sup>	En, Ex		Memon <i>et al.</i> 2007
Methyl parathion	Watermelon peels	110 C	Nitric acid	L	7	1 <sup>st</sup>	En	Acidic pH gives higher adsorption.	Memon <i>et al.</i> 2008
Methyl parathion	Mango kernels	110 C	Nitric acid	L	-	1 <sup>st</sup>	En		Memon <i>et al.</i> 2009
Polychlorinated biphenyl (PCBs)	Granular active carbon	AC	-	-	-	-	-	Biofilm adversely affected adsorption of PCBs, but not considered significant.	Mercier <i>et al.</i> 2013
Ibuprofen	Active carbon fr. cork waste	AC	K <sub>2</sub> CO <sub>3</sub> , steam	L	139-417	2 <sup>nd</sup>	nul	Removal decreases with increasing pH; best with oxidation then steam activation.	Mestre <i>et al.</i> 2007
Chlorhexidine diacetate	Flax fibers, Cotton fibers	Yes	Bleach, Cottoniz		0.4, 0.2	-	-	The low porosity and high crystallinity of the cellulose explains the low adsorption.	Mikhailovska <i>et al.</i> 2012
Trichloroethylene	Active carbon 3 commercial	AC	-	-	200-450	-	-	Air stripping was reduced by water vapor.	Miyake <i>et al.</i> 2003

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Pyridine	Active carbons (coconut)	AC	H <sub>2</sub> SO <sub>4</sub> 200-800	L	20-161	1 <sup>st</sup>	En	Best uptake at pH>4; film diffusion	Mohan <i>et al.</i> 2004
Alpha-picoline, Beta-picoline, Gamma-picline	Active carbons (coconut)	AC	H <sub>2</sub> SO <sub>4</sub> 200-800	L	25-49; 42-149; 142-400	2 <sup>nd</sup>		Particle diffusion or film diffusion; adsorption capacities were inconsistent relative to temperature of equilibration.	Mohan <i>et al.</i> 2005
Phenol	Active carbons (sawdust)	AC	ZnCl <sub>2</sub> 300-600	L F	3	2 <sup>nd</sup>	-	Highest uptake at pH=3.5	Mohanty <i>et al.</i> 2005
Pentachlorophenol	Granular active carbon	AC	-	RP F	500	-	Ex	Radke-Prausnitz modified isotherm accounts for both pH and temperature; desorbable at high pH.	Mollah & Robinson 1996a
Pentachlorophenol	Granular active carbon	AC	-	-	-	1 <sup>st</sup>	-	Batch and plug-flow kinetics modeled.	Mollah & Robinson 1996b
Phenol, <i>m</i> -Aminophenol, <i>p</i> -Cresol, <i>p</i> -Nitrophenol	Active carbon fr. coal	AC	Steam	-	167, 178, 209, 196	-	-	Thermal regeneration was possible, but the adsorption capacities gradually decreased with increasing cycles; some was physi- and some chemi-sorbed.	Moreno-Castilla <i>et al.</i> 1995a
Phenol, <i>m</i> -Aminophenol, <i>p</i> -Cresol, <i>p</i> -Nitrophenol, <i>m</i> -Chlorophenol	Active carbon fr. coal	AC	Steam	L	97-152, 66-183, 99-243, 127-232, 66-206	-	-	Donor-acceptor interactions; adsorption fell at higher pH, depending on adsorbate details.	Moreno-Castilla <i>et al.</i> 1995b
Phenol, <i>p</i> -Nitrophenol	Active carbon	AC	Nitric a., CO <sub>2</sub>	L	73-238	-	-	The pH effects were consistent with charge interactions.	Mourão <i>et al.</i> 2011
Phenol	Charred sawdust	BC	673C	L	345	2 <sup>nd</sup>	-	Oxygen-containing groups participated in the adsorption.	Mubarik <i>et al.</i> 2012
Analine, Benzoic acid, <i>p</i> -Nitrophenol	Activated carbon	AC	-	L	465-660, 866, 695-987	-	-	Accounting for pH effects by means of pK <sub>a</sub> values and double layer effects	Müller <i>et al.</i> 1985a



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Phenol	Activated carbons	AC	Nitric a., CO <sub>2</sub>	F	45-90	-	-	Reduced adsorption at high pH due to electrostatics; pi-pi interactions proposed.	Nabais <i>et al.</i> 2009
Phenol	<i>Pseudomonas aeruginosa</i>	-	Free or fixed	-	-	-	-	Fixing of the bacteria onto GAC or on alginate beads doubles the adsorption.	Namane <i>et al.</i> 2012
2-Chlorophenol	Carbon from coir pith	AC	700C	F	18	2 <sup>nd</sup>		Acidic pH favored adsorption; chemisorption played major role.	Namasivayam & Kavitha 2003
Phenol	Carbon from coir pith	AC	ZnCl <sub>2</sub> 700C	LF	-	-	-	Rate of adsorption was faster for smaller particles.	Namasivayam & Sangr. 2006
Paraquat	Sawdust from <i>Triplochiton s</i>	Sun dry	Ground	L	9.5	2 <sup>nd</sup>	Ex	Uptake increases with increasing pH; NaCl reduces adsorption capacity.	NanseuNjiki <i>et al.</i> 2010
2-Nitrophenol, 2-Chlorophenol	Seaweeds (algae)	60C	Ground CaCl <sub>2</sub>	L F	19-97, 10-24	-	-	Hydrophobicity (octanol partitioning coef.) explained the main results.	Navarro <i>et al.</i> 2009
Phenol	Seaweeds (algae)	60C	Ground CaCl <sub>2</sub>	-	-	-	-	Higher uptake at pH=10; proposes hydrogen bonding concept.	Navarro <i>et al.</i> 2008
Phenol	<i>Posidonia oceanica</i>	40C	1-2 mm selected	RP	5	2 <sup>nd</sup>	-	Adsorption onto seagrass highest at pH=5.	Ncibi <i>et al.</i> 2006
p-Chlorophenol, 3,4-Dichlorophenol, 2,4,6-Trichlorophen.	Granular active carbon	AC	-	LF	2, 3, 3	-	Ex	Particle size affected rate but not capacity; thermal regeneration was effective; uptake drops with increasing pH above 7.	Nelson & Yang 1995
Phenol, Nonylphenol	Active carbons	AC	HNO <sub>3</sub> optional	-	150-225, 440-620	-	-	Oxidation caused 2-step adsorption; authors proposed hydrogen bonding.	Nevskaia & G.-R. 2001
Nonylphenol	Active carbons	AC	-	-	260-725	-	-	Two-step isotherms were attributed to micropores and "surface micelles".	Nevskaia <i>et al.</i> 2001
2-Methylisoborneol, Nat. organic material	Active carbons (six types)	AC	-	-	-	-	-	Pre-adsorption of 2-methylisoborneol did not affect NOM subsequent adsorption.	Newcombe <i>et al.</i> 2002a
2-Methylisoborneol, Nat. organic material	Active carbons (six types)	AC	-		0.2-10	-	-	Pore blockage by NOM	Newcombe <i>et al.</i> 2002b

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
<i>Trans</i> -1,10-dimethyl- <i>trans</i> -9-decalol	Active carbons fr. ag. residue	AC	Steam	F	-	-	-	Adsorption of "geosim" onto active carbons from bagasse & pecan shell	Ng <i>et al.</i> 2000
Cinnamic acid salt, Coumaric acid salt	Biochar (carbon black)	BC	-	L	10-23, 20	-	-	Release of ions upon adsorption implies an ion exchange mechanism.	Ni <i>et al.</i> 2011
3-Chlorophenol, 2,4-Dichlorophenol, 3,4-Dichlorophenol, 2,4,6-Trichlorophen., Pentachlorophenol	Anaerobic sludge granules from a CTMP paper mill	Live	Acclimation	-	-	-	-	Packed bed experiments; linear adsorption behavior was observed; biosorption slowed the elution of the phenols through the column.	Ning <i>et al.</i> 1999
<i>p</i> -Nitrophenol	Activated carbon	AC	Untreat., H <sub>2</sub> , urea, H <sub>2</sub> SO <sub>4</sub>	L	63-210, 83-180, 63-180, 42-250	-	-	Higher uptake at low pH	Nouri & Haghseresht 2004
Benzene, Toluene, <i>p</i> -Cresol, Benzoic acid	Activated carbon	AC	-	L	275-275, 274-278, 176-217, 29-248	-	-	Increased uptake with decreasing pH in cases of benzoic acid and cresol; results were consistent with pK <sub>a</sub> values.	Nouri & Haghseresht 2005
<i>p</i> -Cresol, <i>p</i> -Nitrophenol	Activated carbon	AC	-	L	122-174, 67-224	-	-	Adsorption depended on solubility, which depended on the pH and dissociation.	Nouri <i>et al.</i> 2002a
Perfluorinated surfactants	Active carbon, Zeolite, Sludge	AC - -	-	L	60-250, 5-105, 2-120	-	-	Adsorption capacity increased with length of the fluorocarbon tail; activated carbon was most effective.	Ochoa-Herrera & S.-A. 2008
4-Nitrophenol	Sawdust from <i>Mansonia</i>	100	Ground	L	21	2 <sup>nd</sup>	-	Three distinct stages of diffusion	Ofomaja 2011
4-Nitrophenol	Mansonia wood sawdust	100	Water wash	-	16	2 <sup>nd</sup> 1 <sup>st</sup>	-	Multistage adsorption to reduce aqueous concentration to a low level; pH < 6 best	Ofomaja & U. 2011
4-Nitrophenol	Mansonia wood sawdust	100	Ground	L	150-425	2 <sup>nd</sup>	-	Time-dependent Langmuir model shows three stages.	Ofomaja & U. 2013

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4-Chlorophenol	Granular active carbon	AC	Steam	-	80-200	-	-	Bioregeneration was fitted to a Haldane kinetic model.	Oh <i>et al.</i> 2013
4-Chlorophenol, 2,4-Dichlorophenol	Granular active carbon	AC	Steam	-	150-280 100-280	-	-	The highest biodegradation was when the concentration was below acclimated level.	Oh <i>et al.</i> 2011
Trichloroethylene	Granular active carbon	AC	-	F	1-20	-	-	Wet peroxide oxidation used to regenerate the adsorbent, low affinity adsorption.	Okawa <i>et al.</i> 2007
Phenanthrene	Cork	-	Un-treated	-	-	-	-	Hydrophobic interactions attributed to pi-pi stacking; negatively charged groups inhibit adsorption.	Olivella <i>et al.</i> 2013
2,4-D, 2,4-DP, 2,4-DB	<i>Anoxybacillus flavithermus</i>	80C	Ground	L F	24, 14, 14	1 <sup>st</sup>	-	Optimum pH=4	Ozdemir <i>et al.</i> 2012
Phenol	Active carbon	AC	-	L	50	1 <sup>st</sup>	-	NaOH was used for regeneration.	Özkaya 2006
Phenol	Active carbon, Charcoal	AC BC	- 700C	F L	6-18, 41-74	-	-	The biochars adsorbed more phenol as the pH was lowered below 4.	Pajooeshfar & Saeed 2009
14 organic chloro compounds	Active carbon (5 common)	AC	-	F	0.03-43	-	-	The authors found no easy way to predict adsorbed amounts.	Pavoni <i>et al.</i> 2006
1,2-Dichlorobenzene	Carbon nanotubes	-	-	-	28-31	-	En	Good adsorption in range 3<pH<10; falls off at pH=11.	Peng <i>et al.</i> 2003
Phenol	Active carbons	AC	Nitric a, heat	DA	56-132	-	-	Dubinin-Astakhov isotherm was used to quantify heterogeneity of adsorption.	Podkościelny <i>et al.</i> 2003
Pentachlorophenol	Granular active carbon	AC	Plasma (N <sub>2</sub> , O <sub>2</sub> )	-	120-150	-	-	Oxygen plasma slightly increase uptake; N <sub>2</sub> plasma caused a decline.	Qu <i>et al.</i> 2013
1,3-Dinitrobenzene,	Gram+ and Gram-bacteria	Dry	Freeze-dried	L	17-84,	-	-	Increased uptake with increasing pH; proposed n-pi interactions.	Qu <i>et al.</i> 2008
Meth. tertbutyl ether, Trichloroethylene	Activated carbons	AC	Natural organics		0.01-0.8, 0.3-18	-	-	Pores should be 1.5 times the size of the target molecules to avoid blockage.	Quinlivan <i>et al.</i> 2005

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
<i>p</i> -Chlorophenol, 1,4,6-Trichlorophen.	Activated carbons	AC	KOH, etc.	F	73-134, 112-122	2 <sup>nd</sup>	-	Lower pH favored adsorption; only 10-50% desorption, even at pH=11.	Radhika & Pal-anivelu 2006
Aniline, Nitrobenzene	Active carbons	AC	Oxidiz., Heated	-	46-186, 120-490	-	-	Both electrostatic & dispersive forces are important; aniline uptake enhanced by oxidation; nitrobenzene by low O content.	Radovic <i>et al.</i> 1997
Phenanthrene, Naphthalene, 1,3,5-Trichlorobenz, 1,2-Dichlorobenzene	Peats and humic acids	-	-	F	3-360, 10-120, 10-30, 3-30	-	-	The substrate surfaces were highly heterogeneous.	Ran <i>et al.</i> 2013
Phenol	<i>Aspergillus niger</i>	65-70C	H <sub>2</sub> SO <sub>4</sub> best	L	0.3	-	-	Best pH=5, BET isotherm, irreversible uptake	Rao & Viraraghavan 2002
Lindane, Heptachlor	Pine bark	105 C	ground	F	0.1-200	-	-	Low affinity isotherms shown.	Ratola <i>et al.</i> 2003
Phenol, <i>o</i> -Cresol, <i>m</i> -Cresol, <i>p</i> -Cresol, Benzyl alcohol	Active carbon	AC	-	L	410-600, 420-460, 330-370, 380-480, 340-460	-	nil	Irreversibility of adsorption implies changes in adsorbates upon adsorption.	Ravi <i>et al.</i> 1998
Phenol	Active carbon fr. palm seed	AC	CO <sub>2</sub> 850-900	F	2-20	-	-	Decreased uptake below pH 3 and above pH=10, film diffusion rate control	Rengaraj <i>et al.</i> 2002a
Phenol	Active carbon fr. rubber seed	AC	CO <sub>2</sub> 850-900	F	10-15	1 <sup>st</sup> ID	-	Batch and column; intraparticle diffusion control	Rengaraj <i>et al.</i> 2002b
2-Chlorophenol, 3-Chlorophenol	Active carbons (various)	AC	- 840	L	218-401, 218-394	-	-	Low pH favors adsorption; agricultural-derived active carbons were highly effective; uptake related to pore volume.	Rivera-Utrilla <i>et al.</i> 1991
Phenol	Active carbon fr. avocado	AC	CO <sub>2</sub> 900C	L	87	2 <sup>nd</sup>	nil	Best pH 4 to 8.5, proposes pi-pi interaction, no easy regeneration found.	Rodrigues <i>et al.</i> 2011

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Penol	Active carbon fr. macademia	AC	CO <sub>2</sub> 850C	L	341	2 <sup>nd</sup>	Ex	Decreased uptake with increasing pH.	Rodrigues <i>et al.</i> 2013
Linuron, Alachlor, Metalaxyl, Chlorpyrifos, Dicamba, Paraquat	Nine types of wood with lignin 18 to 27% content	-	Ground	F	>10, >1, >0.2, >3, >5 >30	-	-	Strong correlation between uptake and lignin content; the bulk concentrations were too low to provide reliable isotherms and adsorption capacities.	Rodriguez-C. <i>et al.</i> 2007
Imidacloprid pesticide	<i>Plantago major</i> L.	Dry	As-is		0.002-0.037	-	-	Phytoremediation; gram-positive bacteria were able to induce biodegradation.	Romeh 2010
Phenol	Active carbon, <i>etc.</i>	AC	-	L LF	205-310	1 <sup>st</sup>	Ex	Activated carbon had higher capacity than silica gel, which had the highest rate; smaller particles gave faster adsorption.	Roostaei & Tezel 2004
Meth. tert-butyl ether (MTBE)	Granular active carbon (coconut), <i>etc.</i>	AC	-	F	0.1-30	-	-	Surface diffusion was faster for carbon, compared to other adsorbents; zeolite had higher capacity & costs less to regenerate.	Rossner & Knappe 2008
Endocrine disruptor, pharmaceuticals	Granular active carbon (coconut), <i>etc.</i>	AC	-	-	-	-	-	Heterogeneity of pore size is essential to achieve broad-spectrum adsorption; active carbon removed 24 of the 25 chemicals.	Rossner <i>et al.</i> 2009
Phenol, 2-Chlorophenol, 4-Chlorophenol	<i>Sargassum muticum</i>	60C	CaCl <sub>2</sub> pretreat	L	4.6, 79, 251	1 <sup>st</sup>	-	Uptake correlated with octanol-water partition coefficients, which suggests the importance of hydrophobicity.	Rubin <i>et al.</i> 2006
<i>p</i> -Nitrophenol	Active carbons	AC	-	L	90-185	-	-	CO <sub>2</sub> gasification was much more effective for regeneration than other media.	Sabio <i>et al.</i> 2004
Trichloroethylene, Tetrachloroethylene	Active carbon fibers	AC	-	L	52-150, 130-390	-	-	Key attributes were micropore content (for capacity) and length of diffusion path.	Sakoda <i>et al.</i> 1987

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Phenol	Active carbons from wood	AC	H <sub>3</sub> PO <sub>4</sub> 627C 1027C	F	50-300	-	-	Phenol uptake depends on both porosity and chemistry details; esterification with the surface; COOH reduces pi interaction.	Salame & Bandosz 2003
Phenanthrene	Natural organic matter	-	-	F	10-20	-	-	Lowest phenanthrene uptake on cellulose; highest on paraffinic matter	Salloum <i>et al.</i> 2002
2,4-Dichlorophenol	Active carbon from corn cob	AC	700C	L	18	2 <sup>nd</sup>	-	Acidic pH favored adsorption; incomplete desorption indicated chemisorption.	Sathishkumar <i>et al.</i> 2009
Carbaryl	Carbon from banana pith	AC	ZnCl <sub>2</sub> 110C	L F	46	1 <sup>st</sup> 2 <sup>nd</sup>	-	Highest uptake at pH=11, desorption complete with acetone.	Sathishkumar <i>et al.</i> 2008
Phenol, o-Chlorophenol, p-Chlorophenol, 2,4,6-Trichlorophen.	Polyamide hollow fibers with reactive green dye	-	-	-	146, 203, 194, 179	2 <sup>nd</sup>	-	Decreasing sorption with increasing pH above 6; chemisorption may be rate-determining step; regeneration achieved.	Şenel <i>et al.</i> 2006
Refractory organics in 2 <sup>nd</sup> ary wastewater	Bio-activated carbon	-	Innoc.	F	9-16	-	-	Biofilm increased sorption capacity by a factor of four.	Seo <i>et al.</i> 1997
Dibenzothiophenes	Active carbons	AC	800C	F	1-15	-	-	Micropores appeared to be the main site of adsorption.	Seredych & Bandosz 2010
Dibenzothiophenes; 4,6-Dimethyldibenz.	Active carbons	AC	650, 800C	-	20, 33	-	-	Sulfur on the adsorbent promoted uptake of the sulfur-containing compounds.	Seredych & Bandosz 2011
2,4-Dichlorophenol, 2,4,5-Trichlorophen.	SW kraft fiber, & kraft lignin	not,	$\kappa = 5$	-	120-185	-	Ex	Drastic drop in sorption above pH=6; Lignin is mainly responsible for the interaction with wood pulp.	Severtson & Banerjee 1996
Dichloroethylene	Active carbon fiber	AC	Steam 830C	-	4-10	-	-	Reduced metal on the carbon enhanced dichloroethylene uptake.	Shen <i>et al.</i> 2006
o-Cresol, p-Nitrophenol	Fly ash	FA	Al(NO <sub>3</sub> ) <sub>3</sub> & FeCl <sub>3</sub>	-	3-5, 7-10	1 <sup>st</sup> ID	-	Somewhat faster sorption onto smaller particles; intraparticle diffusion; trivalent metal ions became bound to phenolates.	Singh & Rawat 1994a

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Phenol, <i>o</i> -Cresol, <i>m</i> -Cresol, <i>p</i> -Cresol, <i>o</i> -Nitrophenol, <i>m</i> -Nitrophenol, <i>p</i> -Nitrophenol	Fly ash	FA	Al(NO <sub>3</sub> ) <sub>3</sub> & FeCl <sub>3</sub>	L F	4-7, 3-5, 4-6, 5-7, 6-7, 7-8, 8-10	-	-	Higher capacity with decreasing particle size; trivalent metal species boosted adsorption by about 20%.	Singh & Rawat 1994b
Phenol, 2,4-Dichlorophenol	Active carbons from coconut	AC	H <sub>2</sub> SO <sub>4</sub> 200-800	L F	300-490, 310-650	2 <sup>nd</sup>	En	Sulfuric acid activation enhanced adsorption.	Singh <i>et al.</i> 2008
Pentachlorophenol	Active carbon	AC	-	F	-	-	-	Fixed beds, surface diffusion model	Slaney & Bhamidim. 1998
Phenol, <i>p</i> -Nitrophenol	Active carbon	AC	-	F	180-380		nil	Adsorption heterogeneity and hysteresis observed, intermediate pH is favored.	Snoeyink <i>et al.</i> 1969
Phenol	Cotton with acrylate graft	-	-	-	-	-	-	Sulfonic acid modification of the grafted cotton gave high adsorption of phenol.	Sokker <i>et al.</i> 2009
Ethylene	Active carbon in paper	AC	10-30% content	-	0.0004-0.0008	-	-	Glucomanan did not affect ethylene uptake.	Sothornvit & S. 2012
2,4,6-Trinitrophenol, 4-Nitrophenol, 4-Chlorophenol, 1,3-Dihydroxybenzene.	Active carbon fr. fertilizer	AC	450	L	183, 74, 59, 37	-	-	Competitive adsorption was significant.	Srivastava & Tyagi 1995a
of 2,4-Dinitrophenol	Active carbons fr. fertilizer	AC	450C HCl	L	114-129	-	-	Optimum pH=4; salt increased uptake; complete desorption with NaOH; regeneration with HNO <sub>3</sub> .	Srivastava <i>et al.</i> 1997
Phenol	Fly ash, Active carbons	FA	-	RP L	24, 25-30	2 <sup>nd</sup>	En	Best results at pH=6.5	Srivastava <i>et al.</i> 2006

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Phenol, <i>p</i> -Nitrophenol	Olive pomace	Dry	Dried, Extract.	L F	5-11	2 <sup>nd</sup>	-	Uptake increased with increasing pH.	Stasinakis <i>et al.</i> 2008
Phenol	Active carbons	AC	O <sub>2</sub> , HNO <sub>3</sub> , Urea	F	50-440			Nitrogen groups from urea favored adsorption of phenol; oxygen groups reduced uptake.	Stavropoulos <i>et al.</i> 2008
Pyrene, Phenanthrene	Mixed microbes	-	-	-	-	-	-	Partition coefficients octanol/water predicted uptake.	Steen & Karickhoff 1981
Phenol, 3-Chlorophenol	Active carbon	AC	-	DRK L	120-350, 75-450	-	-	Monolayer adsorption; the Dubinin-Radushkevich-Kaganer (DRK) equation is based on BET surface area & energy term.	Stoeckli <i>et al.</i> 2001
Phenol, <i>p</i> -Chlorophenol	Active carbon fr. straw, <i>etc.</i>	AC	Steam 800-900	F	113-193, 116-335	-	-	Results were as good as commercial activated carbon products.	Streat <i>et al.</i> 1995
Phenanthrene	Bacterial biomass	no	CH <sub>2</sub> O to kill cells	-	3	-	-	Nocardioform bacteria exhibited the highest adsorption.	Stringfellow & Alvarez-C 1999
Phenol	Active carbon fr. coir pith	AC	ZnCl <sub>2</sub> 700C	L	93	2 <sup>nd</sup>	nil	Desorption increased with increasing pH.	Subha & Namasivayam 2009
2-Chlorophenol	Active carbon fr. coir pith	AC	ZnCl <sub>2</sub> 700C	L	149	2 <sup>nd</sup>	nil	Only partial desorption took place, even at the very highest pH of 14.	Subha & Namasivayam 2010
Phenol	Granular active carbon	AC	-	L	67	-	-	Packed bed and competitive adsorption with lead	Sulaymon <i>et al.</i> 2012
Phenol	Active carbon, Anaer. sludge	AC -	- Dried	L	67, 70	-	-	Competition was observed between phenol and lead.	Sulaymon <i>et al.</i> 2013
Fluridone pesticide, Norflurizon pesticide	Biochar, Soil organics	BC -	250-400 HCl	F	5, 5	-	-	Aliphatic and aromatic components and nitrogen were important for adsorption.	Sun <i>et al.</i> 2012a
Di-ethyl phthalate, Di-butyl phthalate, Butylbenzyl phthal.	Biochars	BC	300-400	F	1-60, 1-50, 2-60	-	-	Uptake correlated to hydrophobicity of the sorbate	Sun <i>et al.</i> 2012b



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Fluridone pesticide, Norflurizon pesticide	Biochars	BC	200-600	F	1-60, 1-80	-	-	Lower-temperature treatment yielded (400) higher sorption; aromatic content was key.	Sun <i>et al.</i> 2011a
Bisphenol A, 17 $\alpha$ Ethinylestradiol, Phenanthrene	Biochars	BC	Therml, Hydroth. 250;400	F	0.1-20, 0.1-8, 0.2-20	-	-	Hydrothermal chars are more amorphous, giving wider spectrum of adsorption; low affinity results.	Sun <i>et al.</i> 2011b
2,4,6-Trichlorophen.	Active carbon fr. corn husk	AC	KOH, CO <sub>2</sub> 750	F	192	-	-	Large-well-developed pores resulted from the optimized activation.	Tan <i>et al.</i> 2008
2,4,6-Trichlorophen.	Active carbon from palm	AC	KOH, CO <sub>2</sub> 750	-	5-9	-	-	Column experiments, breakthrough; ethanol was effective for regeneration.	Tan <i>et al.</i> 2009a
2,4,6-Trichlorophen.	Active carbon from palm	AC	KOH, CO <sub>2</sub> 700	F L	500-588	2 <sup>nd</sup>	En	Lower pH favored, intraparticle diffusion was rate-controlling.	Tan <i>et al.</i> 2009b
Phenol	Active carbons from wood	AC	500	L F	46-148	-	-	Preferential sorption observed onto carbon element, not on the clay binder used.	Tancredi <i>et al.</i> 2004
<i>p</i> -Nitrophenol	Active carbon fiber	AC	-	F	357-385	2 <sup>nd</sup>	En	Adsorption dropped at pH above 6; NaOH desorbed only 60%, regardless of conc.	Tang <i>et al.</i> 2007
Phenol	Active carbons	AC	CO <sub>2</sub>	L F	73-138	-	Ex	Uptake correlated to surface area, but negatively affected by oxygen content.	Teng & Hsieh 1999
Phenol	Microporous carbons	AC	Molec. dynamic	-	-	-	-	Pore of about 0.6 nm are optimal; surface oxygen tends to block such pores.	Terzyk <i>et al.</i> 2010
<i>o</i> -Cresol, <i>o</i> -Chlorophenol	Active carbons	AC	Outgas	F	90-300	-	-	Oxygen-containing surface groups promote irreversible adsorption.	Tessmer <i>et al.</i> 1997
Phenol	Sewage sludge	-	Dried	-	94	-	-	Maximum removal was at pH 6 to 8.	Thawornchaisit & P. 2007
Dieldrin pesticide, Chlorpyrifos	Active carbons	AC	Steam 800+	F	544-910, 500-873	-	-	Favorable pore size distribution was achieved.	Thuy <i>et al.</i> 2012
Phenol	Active carbons from oak cup	AC	H <sub>3</sub> PO <sub>4</sub> ZnCl <sub>2</sub>	L	62 75	-	-	Adsorption mainly was related to micropores.	Timur <i>et al.</i> 2010

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Phenol, o-Cresol	Granular active carbon	AC	Steam	-	150-170, 210-225	-	-	Bioregeneration was shown to be effective.	Toh <i>et al.</i> 2013
Benzene, toluene, acetone, etc. mix	Granular active carbon	AC	H <sub>3</sub> PO <sub>4</sub> CO <sub>2</sub>	-	30-50	-	-	Activation conditions affected uptake of polar and nonpolar adsorbates.	Toles <i>et al.</i> 1997
Benzene, toluene, acetone, etc. mix	Granular active carbon	AC	H <sub>3</sub> PO <sub>4</sub>	-	25-40	-	-	Air oxidation could be used in place of conventional oxidation.	Toles <i>et al.</i> 1998
Phenol,	Active carbons from pine	AC	Steam 900	F	120-170	2 <sup>nd</sup>	-	The Elovich equation could fit the kinetic data best.	Tseng <i>et al.</i> 2003
Phenol, 4-Chlorophenol, 2,4-Dichlorophenol	Active carbons	AC	450C NaOH	L	214-284, 308-426, 438-613	-	-	The process could be divided into fast and moderately fast segments.	Tseng <i>et al.</i> 2010
2,4-Dichlorophenol	Active carbons	AC	NaOH 780	L	719	2 <sup>nd</sup>	-	Half-life and half-capacity values were shown to be useful.	Tseng <i>et al.</i> 2011
Lindane, Pentachlorophenol	Activated sludge	-	Live	F	-	-	-	Biosorption played a significant role.	Tsezos & Bell 1988
Lindane, Diazinon, Pentachlorophenol, 2-Chlorobiphenyl	<i>Rhizopus arrhizus</i>	Dry	Live and dead	F	0.8-1	-	-	Results consistent with octanol/water partition coefficients; drying of the biomass increased uptake by a factor of about 3.	Tsezos & Bell 1989
Malathion	<i>R. arrhizus</i> , Active sludge	No	Live and dead	F	30	-	-	Either living or dead cells were able to biosorb the pollutant; reversible sorption.	Tsezos & Bell 1991
Lindane, Diazinon, 2-Chlorobiphenyl	<i>R. arrhizus</i> , Active sludge	115 C	-	-	-	2 <sup>nd</sup>	-	Reversibility shown	Tsezos & Wang 1991b

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Tetrachloroethylene, Trichloroethylene, 1,2-Dichloroethylen, 1,1-Dichloroethane, Carbontetrachloride, Trichloroethane, Chloroform	Granular active carbons	AC	-	F	1-100	-	-	Pores smaller than 2 nm had a dominant effect; humic substances decreased sorption by about 10-20%.	Urano <i>et al</i> 1991
2-Methylpehnol,	Active carbons	AC	Anoxic, Oxidiz.	-	79-142, 105-288	-	-	Irreversible adsorption (up to 288 mg/g) was proportional to surface area.	Uranowski <i>et al.</i> 1998
Phenols mixture	Granular active carbon	AC	-	L F	1.5	1 <sup>st</sup>	-	Column experiments	Vázquez <i>et al.</i> 2007
2-Methylphenol, 2-Chlorophenol, 2-Ethylphenol	Granular active carbon	AC	Anoxic, Oxidiz.	F	100-300, 250-400	-	-	Oxygenation increased the adsorption capacity.	Vidic <i>et al.</i> 1994
Phenol, Analine, Nitrobenzene	Active carbons	AC	HNO <sub>3</sub> H <sub>2</sub>	L	103-179, 105-214, 197-406	-	-	The aminated carbon exhibited the highest sorption capacity.	Villacanas <i>et al.</i> 2006
Phenol	Peat, Fly ash, Bentonite	103, - -	-	F, L	0.2, 40	-	-	Optimum pH 3 to 5.	Viraraghavan & Alfaro 1998
2,4,6-Trinitrophenol, 4-Nitrophenol, 2,4-Dinitrophenol,	Acrylate-graft cotton	-	Glycicyl meth-acrylate	L F	56-116, 31-65, 56-108	2 <sup>nd</sup>	-	Poor adsorption at pH 2.3 in most cases; most data are for pH 11; glycidic groups favored uptake of hydrophobic compound.	Vismara <i>et al.</i> 2009

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
2,4-Dichlorophenol	Active carbon fibers	AC	StaticAir 900C	L RP	396-400	-	-	Lower pH is favorable, pi-pi interactions & electrostatics; use NaOH to regenerate.	Wang <i>et al.</i> 2007a
2,4-Dichlorophenol	Active carbon fibers	AC	StaticAir 900C	L	342-372	2 <sup>nd</sup>	Ex	Air activation was judged to be an efficient approach.	Wang <i>et al.</i> 2007b
Di-n-butyl phthalate	<i>Pseudomonas fluorescens</i>	Auto clav	Live vs. dead	F	1.7, 2.5	-	-	Dead biomass had a higher affinity.	Wang & Grady 1994
Perchloroethylene, Trichloroethylene, Trans-dichloroethyl., Cis-dichloroethylene	Pine mulch, Hardwood m., Cypress mulch	60C	Wash, auto-clave	L F	92-320, 162-315, 94-102, 88-150			Pine mulch was most effective.	Wei & Seo 2010
<i>p</i> -Nitrophenol	Active carbon	AC	-	-	-	-	-	Fixed bed breakthrough curves	Wolborka 1989
Phenol, <i>p</i> -Cresol, <i>p</i> -Chlorophenol, <i>p</i> -Nitrophenol	Active carbon fr. fir wood	AC	KOH CO <sub>2</sub> 780	L	220-275, 254-333, 355-418, 377-542	Elo vic.	-	CO <sub>2</sub> played a critical role in activation after the KOH treatment.	Wu & Tseng 2006
Phenol	Active carbon from bamboo	AC	700-880	L	223-231	-	-	Activation conditions were optimized.	Wu <i>et al.</i> 1999
2,4-Dichlorophenol, 4-Chlorophenol, <i>p</i> -Cresol, Phenol	Active carbon from fir wood	AC	KOH Steam	-	244-570, 194-452, 108-324, 94-207	-	-		Wu <i>et al.</i> 2005
4-Chlorophenol	Active carbon fr. corn hull	AC	H <sub>2</sub> SO <sub>4</sub> KOH 780	L	520	Elo vic.	-	Rapid adsorption was attributed to the thin nature of the material.	Wu <i>et al.</i> 2011
Phenol, 2-Chlorophenol, 4-Chlorophenol, 2,4-Dichlorophenol	<i>Phanerochaet. chrysosporium</i> fungal mycelia	Auto clav.	Pellets	F	1, 1.6, 1.7, 3.7	-	-	Results were consistent with octanol-water partitioning coefficients.	Wu & Yu 2006a

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
2,4-Dichlorophenol	<i>Phanerochaet. chrysosporium</i> fungal mycelia	Auto clav.	Pellets	F L	4.1	2 <sup>nd</sup> ID	Ex	Best pH=5, intraparticle diffusion	Wu & Yu 2006b
2,4-Dichlorophenol	<i>Phanerochaet. chrysosporium</i> fungal mycelia	Auto clav.	Immobilized	L F	4-7	-	-	Reversible with distilled water	Wu <i>et al.</i> 2007
2,4-Dichlorophenol	<i>Phanerochaet. chrysosporium</i> fungal mycelia	Auto clav.	Immobilized	-	5-12	-	-	Fixed bed, breakthrough models, the bed could be reused five times with up to 68% desorption.	Wu & Yu 2008
1-Naphthol	MW carbon nanotubes	-	KMnO <sub>4</sub> , NaOH, H <sub>2</sub> SO <sub>4</sub>	-	20-1200	-	-	Oxidative polymerization of the adsorbate; surface oxygen groups covalently bond; adsorption increased up to pH=7, then fell.	Wu <i>et al.</i> 2012a
Phenol	Active carbon (N-enriched)	AC	KOH 850C	L	207	2 <sup>nd</sup>	-	Nitrogen-enriched activated carbon was effective for adsorption of phenol.	Wu <i>et al.</i> 2012b
Phenol, 2-Chlorophenol, 4-Chlorophenol, 2-4-Dichlorophenol	MW carbon nanotubes	-	Zero-valent Fe	L	4, 14, 14, 20	-	-	Chlorine atoms on nanotubes increase adsorption capacity.	Xu <i>et al.</i> 2012
Organochlorines in pulp bleach effluent	Sewage sludge	Auto clav.	-	L F	7.5 as Cl	-	-	Adsorption was not dependent on cell viability.	Yan & Allen 1994
Naphthalene, Phenanthrene, Pyrene	Fullerenes, SW C nanotu., MW C nanot.	-	-	F	1-50, 10-40, 10-45	-	-	Polanyi model was used to fit the isotherms.	Yang <i>et al.</i> 2006
Triphenyltin	<i>Brevibacillus brevis</i>	live	Cultured	-	-	-	-	Endocrine disruptor was biodegraded to certain byproducts; minor pH effects.	Ye <i>et al.</i> 2013

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Trichloroethene, Tetrachloroethene, Trichloroethane, I,I-Dichloroethene	Active carbon fiber	AC	-	-	20-43, 38-88, 4-28, 6-19	-	-	Groundwater purification (closed vinyl chloride plant) was achieved by passing through stirred vessels.	Yu & Chou 2000
Perfluorooctane sulfonate & P. octanoate	Activated carbon, Act. sludge	AC Not	- -	F F	150-250 150-250	-	-	The adsorbed amount fell by half in the presence of effluent organic matter.	Yu & Hu 2011
Methylcyclohexane, Toluene, Isobut.-meth. ketone	Active carbon	AC	-	L	205, 190, 258	-	-	Various isotherms compared.	Yu & Neretnieks 1990
Perfluorooctane SO <sub>4</sub> Perfluorooctanoate	Active carbons	AC	-	L	185-520, 161-1209	2 <sup>nd</sup>	-	Ion exchange and hydrophobic interactions	Yu <i>et al.</i> 2009
Napoxen, Carbamazepine, Nonylphenol	Active carbon	AC	-	F	0.2-1	-	-	Affinities did not match hydrophobicities or capacities; natural organic matter (NOM) suppressed adsorption.	Yu <i>et al.</i> 2008
Phenol (DMSO & acrylonitrile-aq. sys.)	Cellulose	-	H <sub>2</sub> O-organics	-	1-35	-	-	Adsorption on cellulose was affected by adsorbate-solvent interactions; low affinity with evidence of self-association (admicelles) at high bulk concentration of phenol.	Zakharov <i>et al.</i> 2010
Toluene, Dichloromethane	Granular active carbon	AC	-	L	4-9, 340	-	En	A Langmuir-BET model best fit with data for toluene; breakthrough predicted.	Zeinali <i>et al.</i> 2012
Phenanthrene	Pure algae, Field plankton Market algae	dry	Freeze-dried	F	1-10	-	-	Alkyl and nonhydrolyzable components accounted for uptake.	Zhang <i>et al.</i> 2013
Simazine herbicide	Biochars from corn straw	BC	100-600	F	0.1-5	-	-	Aromatic function and pi-pi interactions were important; increased carbonation beneficial; pore-filling mechanism.	Zhang <i>et al.</i> 2011a

Pollutant	Sorbent	Dried, never, heat	Modification	Isotherm best fits	Adsorp. capac. (mg/g)	Rate law best fit	Thermodynamics	Key Findings	Author (year)
Olaquinox (animal growth promoter)	MW carbon nanotubes	-	-	L	133	2 <sup>nd</sup> ID	Ex	Pi-pi interactions; intraparticle diffusion	Zhang <i>et al.</i> 2011b
Naphthylamine, Naphthol, Benzoic acid, <i>p</i> -Toluidine, <i>p</i> -Cresol, <i>p</i> -Toluic acid, Phenol, <i>p</i> -Toluenesulfonic ac	<i>Penicillium oxalicum</i>	Auto clav	Cultured	L F	21, 8, - 3.5, 2.4, -, 0.9, 0.8	-	-	Adsorption was favored by low pH; four key binding sites were identified as carboxyl, phosphoric, amine, and hydroxyl groups; low ionization degree and hydrophobicity favored adsorption.	Zhang <i>et al.</i> 2011c
Sulfamethoxazole antibiotic	Biochars	BC	300-600	F	1-4	F DA	-	Increasing char temp increased uptake; Freundlich/Dubin-Ashtakhov hybrid model; charge-assisted hydrogen bonding can be significant at higher pH values.	Zheng <i>et al.</i> 2013
Atrazine pesticide, Simazine pesticide	Biochar from greenwaste	BC	450C	F	0.4-1.2, 0.2-1.1	-	-	Competitive adsorption effects observed.	Zheng <i>et al.</i> 2010
Phenol	Active carbon fr. vinegar lees	AC	CO <sub>2</sub> 875	L	92-127	-	-	The temperature of activation was optimized.	Zhong <i>et al.</i> 2012

(See notes for Table A on the following page.)

**NOTES FOR TABLE A****Dried, Never, Heat**

AC = Activated carbon (drying is implied in the manner of preparation)

BC = Biochar (drying is implied in the manner of preparation)

C = Degrees Celsius (even if no “C” is shown due to lack of space)

Dry = Dried by some means, temperature not specified

FA = Fly ash, which often is dominated by mineral components after incineration of biomass

FD = Freeze-dried using vacuum

No = Not dried

**Isotherm best fits**

F = Freundlich isotherm gave a good fit to the data.

L = Langmuir isotherm gave a good fit to the data.

RP = Redlich-Peterson isotherm gave a good fit to the data.

T = Temkin isotherm gave a good fit to the data.

**Rate law best fit**

1<sup>st</sup> = Lagergren’s pseudo-first order rate model

2<sup>nd</sup> = Ho and McKay’s pseudo-second order model

ID = Intraparticle diffusion

UT = Urano-Tachikawa model

**Thermodynamics**

En = Endothermic

Ex = Exothermic

nil. = No clear thermal trend