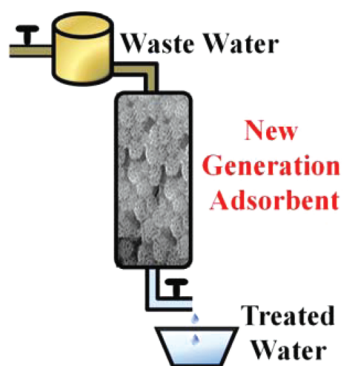


## New Generation Adsorbents for Water Treatment

Imran Ali\*

Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi-110025, India



### CONTENTS

1. Introduction	5073
2. Adsorption	5074
3. Preparation and Characterization of Nanoparticles	5074
4. Water Treatment by Adsorption on Nanoparticles	5074
4.1. Removal of Inorganic Pollutants	5075
4.1.1. Arsenic	5076
4.1.2. Cadmium	5077
4.1.3. Chromium	5077
4.1.4. Cobalt	5078
4.1.5. Copper	5078
4.1.6. Selenium	5078
4.1.7. Miscellaneous Metal Ions	5079
4.1.18. Anions	5079
4.2. Removal of Organic Pollutants	5079
4.2.1. Dyes	5079
4.2.2. Pesticides	5080
4.2.3. Hydrocarbons	5080
4.3. Removal of Biological Pollutants	5080
4.3.1. Viruses and Bacteria	5080
4.4. Applications of Nanotubes	5082
5. Separation of Nanoparticles	5083
6. Regeneration of Nanoparticles	5084
7. Nanotoxicology	5085
8. Future Perspectives of Nanoparticles	5085
9. Conclusion	5086
Author Information	5086
Corresponding Author	5086
Notes	5086
Biography	5087
Acknowledgments	5087
Abbreviations	5087
References	5087

### 1. INTRODUCTION

Water is the most important and essential component on the earth for vital activities of living beings. Unfortunately, water quality of our water resources is deteriorating continuously due to geometrical growth of population, industrialization, civilization, domestic, and agricultural activities, and other geological and environmental changes.<sup>1–3</sup> Therefore, water pollution has become a serious issue in the present scenario, affecting all living creatures, household, recreation, fishing, transportation, and other commercial activities.<sup>4–6</sup> The government authorities, scientists, and academicians are worried and serious on this issue. Thousands of organic, inorganic, and biological pollutants have been reported as water contaminants.<sup>7</sup> Some of them have serious side effects and toxicities with a few being lethal and carcinogenic.<sup>8–10</sup> These pollutants are very dangerous for all of us, aquatic conditions, and the ecosystem of the earth as a whole.

Some heavy metals are notorious water pollutants with high toxicity and carcinogenicity.<sup>11</sup> Arsenic is known as a deadly poison since ancient time due to its several side effects and lethality. The order of toxicities of arsenic species are arsenite > arsenate > monomethyl arsenic acid (MMA) > dimethyl arsenic acid (DMA).<sup>12–19</sup> Besides, other metal ions such as cadmium, chromium, mercury, selenium, lead, etc. have serious toxicities.<sup>20–25</sup> At higher concentration than permissible limit,<sup>6</sup> cobalt causes vomiting, nausea, asthma, and carcinoma. Besides, cobalt is also responsible for thyroid, gastrointestinal, and liver problems.<sup>26–28</sup> Zinc is required for the growth of human beings, but high concentrations more than the permissible limit [3.0 mg/L, WHO] cause poor growth and mental fever.<sup>29–31</sup> Besides, nitrate, sulfate, phosphate, fluoride, chloride, and oxalate have also some hazardous effects. For example, high concentration of nitrate results into blue babies disease (methemoglobinemia) in children.<sup>32</sup> On the other hand, it is well-known that fluorosis is due to high levels of fluoride in water.<sup>33</sup> It has been reported that high concentrations of other anions such as sulfate, phosphate, chloride, oxalate, etc. change water taste.<sup>6</sup>

Many organic pollutants have been found in different water resources. These belong to various classes such as pesticides, fertilizers, hydrocarbons, phenols, plasticizers, biphenyls, detergents, oils, greases, pharmaceuticals, etc.<sup>3,34,35</sup> The side effects and toxicities of these contaminants are discussed in various books and research articles.<sup>34,36,37</sup> The different types of microbes present in wastewater may be responsible for various diseases. The harmful microbes are virus, bacteria, fungi, algae, amoebas, and planktons. These water pollutants remain either in soluble, colloidal, or in suspended form. These microbes are responsible for causing several illnesses called waterborne

Received: October 24, 2011

Published: June 25, 2012

diseases.<sup>38,39</sup> Because of these sorts of pollution, the surface and groundwater at some places of the world are contaminated and not fit for drinking purposes. By 2020, the global population is expected to reach up to 7.9 billion,<sup>40</sup> and because of this the world may be under great water scarcity. Therefore, the removal of these pollutants from contaminated water is an urgent need for providing disease-free health to our society.

For a few decades, different methods have been developed and used for water treatment.<sup>41–54</sup> The most important methods are screening, filtration, centrifugation, micro- and ultra filtration, crystallization, sedimentation and gravity separation, flotation, precipitation, coagulation, oxidation, solvent extraction, evaporation, distillation, reverse osmosis, ion exchange, electrodialysis, electrolysis, adsorption, etc. Adsorption is considered as one of the suitable water treatment methods due to its ease of operation and the availability of a wide range of adsorbents. Besides, adsorption can also be applied for the removal of soluble and insoluble organic, inorganic, and biological pollutants. Additionally, adsorption can also be used for source reduction and reclamation for potable, industrial, and other water purposes. In spite of these facts, adsorption has certain limitations such as it could not achieve a good status at commercial levels. Probably, it is due to the lack of suitable adsorbents of high adsorption capacity and commercial scale columns. Besides, a single adsorbent cannot be used for all kind of pollutants. The different adsorbents are used for different pollutants. A comparison of adsorption method was carried out with other water treatment technologies. The order of cost effectiveness is adsorption > evaporation > aerobic > anaerobic > ion exchange > electrodialysis > micro- and ultra filtration > reverse osmosis > precipitation > distillation > oxidation > solvent extraction. It was observed that, in spite of some limitations, it will be a good water treatment technology in the near future. Much work has been carried on the removal of different pollutants from water by using adsorption batch modes.<sup>17,18</sup> Initially, activated carbon was used for the removal of pollutants from water, which has been replaced by some cost-effective adsorbents.<sup>55,56</sup> In the last two decades, nanotechnology has developed with its applications in almost all branches of science and technology. In this series, water treatment is not deprived of nanotechnology. Nanosize adsorbents have been prepared and used for the removal of water pollutants. In view of the importance of water quality and emerging utilities of nanotechnology, attempts have been made to discuss various aspects of water treatment by adsorption using nanoadsorbents.

## 2. ADSORPTION

Adsorption is a process in which pollutants are adsorbed on the solid surface. Basically, it is a surface phenomenon and adsorption takes place by physical forces but, sometimes, weak chemical bondings also participate in adsorption process.<sup>57</sup> A molecule (pollutant) adhered to the solid surface is called an adsorbate, and the solid surface as an adsorbent. Adsorption is controlled by various parameters such as temperature, nature of the adsorbate and adsorbent, and the presence of other pollutants along with the experimental conditions (pH, concentration of pollutants, contact time, particle size, and temperature). An equilibrium is established when the concentrations of pollutant adsorbed and in water become constant. The relationship between amounts of pollutant adsorbed and in water; at equilibrium, is called an adsorption isotherm (Figure 1). The adsorption is treated for

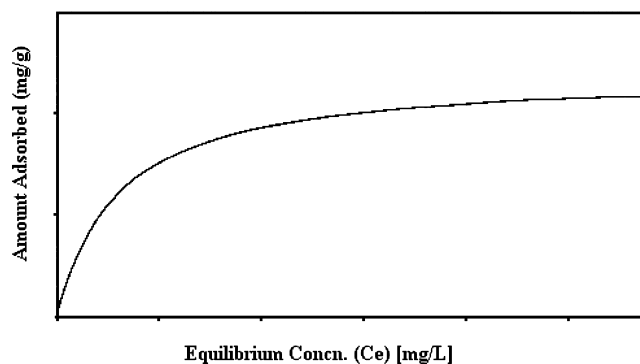


Figure 1. A typical batch adsorption isotherm.

calculation of various adsorption parameters. The important models are Langmuir, Freundlich, Halsey, Henderson, Smith, Elovich liquid film diffusion, intraparticle diffusion, and Lagergren. These are different well-known models used to explain the results of adsorption studies. These models are based on almost similar principle with little difference in their approaches.<sup>58–61</sup> The kinetic study is carried out by calculating enthalpy, free energy, entropy, and energy of activation. The adsorption technology is developed by batch process followed by the column studies. The developed adsorption technology is applied first at pilot and later on industrial scales by using large size columns.

## 3. PREPARATION AND CHARACTERIZATION OF NANOPARTICLES

The preparation and characterization of nanoparticles are the first and foremost steps in water treatment by nanotechnology. The most important methods used for the preparation of nanoparticles include pulsed laser ablation, inert gas condensation, spark discharge generation, spray pyrolysis, ion sputtering, laser pyrolysis, thermal plasma synthesis, photo-thermal synthesis, flame synthesis, flame spray pyrolysis, and low temperature reactive. The composition and molecular structure of the nanoparticles can be modulated through these methods.<sup>62–67</sup> The nanoparticles are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) techniques. Basically, the reported methods are used for the preparation of different types of nanoparticles for various applications such as biomedical, electronics, optical, mechanical, environmental science, etc. The selection of the technique depends on the size, properties, starting materials, and the required applications of nanoparticles. Only those methods are given in Table 1 that have been used for the preparation of nanoparticles for water treatment. For example, the sol–gel method is used for the preparation of nanoparticles of alumina, alumina–silica, cadmium sulfide, maghemite, nickel oxide, titanium oxide, silica, and zinc sulfide. The preparation and characterization of nanoparticles are general topics and not discussed herein, as they are out of the domain of this article. However, interested readers can consult several books on nanotechnology.<sup>68–71</sup> The structures of some commonly used nanoparticles for water treatment are given in Figure 2.

## 4. WATER TREATMENT BY ADSORPTION ON NANOPARTICLES

The particles of 1–100 nm size are called nanoparticles,<sup>72,73</sup> which offer the potential for the treatment of contaminated

Table 1. The Different Methods for Synthesizing Nanoparticles Used As Adsorbents for Water Treatment

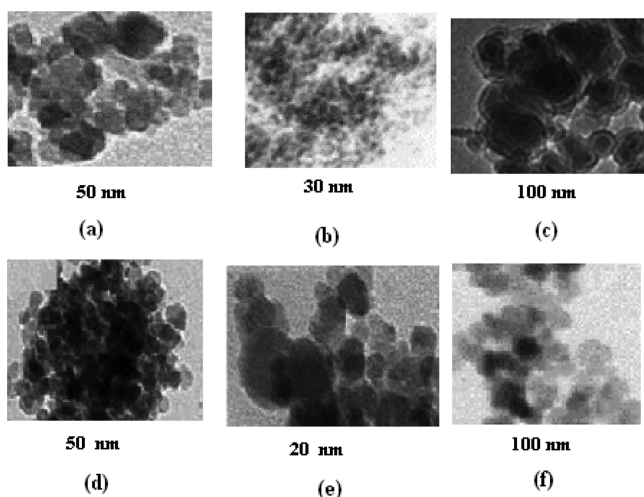
nanoparticles	methods	diameter (nm)	starting material	refs
akaganiete	precipitation method	2.6	iron(III) chloride, ammonium carbonate	109
alumina	sol-gel method	6–30	AlCl <sub>3</sub> ·6H <sub>2</sub> O	208
	sol-gel method	50	aluminum isopropoxide, cyclohexane, NH <sub>4</sub> OH	89
	hydrolysis	80	aluminum isopropoxide, sodium bis-2-ethylhexylsulfosuccinate	209
alumina-silica	sol-gel method	30	tetra ethyl orthosilicate, ethanol, NH <sub>4</sub> OH, 2-propanol, aluminum tri-sec-butoxide	110
anatase	solvothermal method	8–20	titanium(IV) ethoxide, ethanol	108
cobalt ferrite	wet chemical route	15–48	ferric chloride, cobalt chloride, NaOH	112
chromium-doped zinc oxide	chemical vapor synthesis	18	zinc acetyl acetate, chromium acetyl acetate	210
cobalt ferrite	combustion wave	2.7–17	iron nitrate, cobalt nitrate, glycine	211
ceria	flame electrospray pyrolysis	2.4–6	cerium(III) nitrate hexahydrate, ethanol, diethylene glycol butyl ether	212
CuO	reverse micelles	5–25	copper chloride, ammonia, Triton-X-100, <i>n</i> -hexanol, <i>n</i> -pentanol, cyclohexane	213
CdS	sol-gel method	1.66	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> , C <sub>2</sub> H <sub>5</sub> OH, HCl, cadmium acetate, sodium sulphide	214
Gold	sonochemical synthesis	22	NaAuCl <sub>4</sub> , chitosan powder, propan-2-ol, NaBr	215
	photochemical synthesis	7.5	sodium dodecylsulfonate, Au(III) solution, macromolecular polymer, dendrimers	216
	intramolecular photoreduction	6.7–50.9	gold, aquaregia, EDTA, Fe <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	217
gum arabic modified magnetic nanoadsorbant	coprecipitation	13–67	ferric chloride-6-hydrate, gum arabic, ammonium hydroxide	122
iron nickel alloy	reverse micelle technique	4–12	iron(II) chloride, nickel(II) chloride, sodium borohydride, isooctane, <i>n</i> -butanol, cetyl-trimethyl-ammonium-bromide	218
iron oxide	hydrothermal synthesis	14–25	iron sulfate, <i>n</i> -decanoic acid or <i>n</i> -decylamine	219
FeOOH-coated maghemite ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> ) nanoparticles	surface precipitation	15	$\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (nanoscale), ferric salt, NaOH, H <sub>2</sub> O <sub>2</sub>	178
MgAl <sub>2</sub> O <sub>4</sub>	thermal decomposition	10	Al(NO <sub>3</sub> ) <sub>3</sub> ·9H <sub>2</sub> O, Mg(NO <sub>3</sub> ) <sub>3</sub> ·6H <sub>2</sub> O	220
maghemite	sol-gel method	10	FeCl <sub>3</sub> , FeCl <sub>2</sub> , NH <sub>4</sub> OH	112
nanocrystalline titanium dioxide	hydrolysis	6	titanium sulfate	97
NiO nanoparticles	sol-gel synthesis	4–22	nickel acetate tetrahydrate, oxalic acid, ethanol	221
silica	sol-gel method	15–700	Si(OC <sub>2</sub> H <sub>5</sub> ) <sub>4</sub>	222
SnO <sub>2</sub> nanoparticles	precipitation route	20–60	SnCl <sub>2</sub> ·2H <sub>2</sub> O, NH <sub>4</sub> OH	223
TiO <sub>2</sub>	combustion synthesis	100–1000	titanium powder, sodium perchlorate	224
	laser pyrolysis	14	TiCl <sub>4</sub>	225
	solvothermal method	10, 20	Ti(OR) <sub>4</sub> , toluene	226
ZnO	sol-gel method	5	<i>n</i> -butyl-methylimidazolium hexafluoro phosphates [BMIM][PF <sub>6</sub> ]	227
	sonochemical synthesis	70–80	ZnCl <sub>2</sub> , KOH	228
zinc sulfide	sol-gel method	2.3–4.5	tetraethyl orthosilicate, 2-propanol, thioureas, Zn(NO <sub>3</sub> ) <sub>2</sub> ·6H <sub>2</sub> O	229
zinc oxide	laser ablation	14–20	2-propanol, acetone, zinc metal	230
zinc oxide	thermolysis	18–45	zinc nitrate, polyvinyl alcohol	231
zirconia	precipitation method	15	zirconium oxychloride octahydrate, zirconyl chloride, ammonia solution	232

water. Some nanoparticles have been prepared and used for water treatment. Nanoparticles have proven themselves as excellent adsorbents due to their unique features. The most important characteristics of these particles; which made them ideal adsorbents, are small size, catalytic potential, high reactivity, large surface area, ease of separation, and large number of active sites for interaction with different contaminants. These properties are responsible for high adsorption capacities by increasing the surface area, free active valences, and surface energies of nanoparticles. The BET surface area of some important nanoparticles, used in water treatment, are given in Table 2. The commonly used nanoparticles for water treatment are made of alumina, anatase, akaganeite, cadmium sulphide, cobalt ferrite, copper oxide, gold, maghemite, iron, iron oxide, iron hydroxide, nickel oxide,

silica, stannous oxide, titanium oxide, titanium oxide, zinc sulfide, zinc oxide, zirconia, and some alloys.

#### 4.1. Removal of Inorganic Pollutants

The adsorption technology is capable to remove inorganic pollutants from water. The most commonly used nanoparticles for the removal of metal ions are oxides of aluminum, iron, and titanium. Some workers have used nanoparticles of iron oxide for efficient removal of metal ions due to their high surface areas and ease of preparation.<sup>74,75</sup> The different forms of iron oxides used for the purpose are goethite, amorphous ferric oxide, and crystalline ferric oxide.<sup>73–81</sup> Iron oxides have also been used for the removal of copper,<sup>75</sup> arsenic,<sup>82</sup> etc. On the other hand, nanoparticles of zerovalent iron have also been used for sorption of arsenic, cadmium, chromium, silver, selenium, lead, and zinc metal ions.<sup>83–85</sup> Besides, nanoparticles



**Figure 2.** TEM images of some nanoparticles with their sizes. (a) maghemite, (b) akaganeite, (c) zerovalent iron, (d)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>, (e)  $\delta$ -FeOOH, and (f) chitosan bounded Fe<sub>2</sub>O<sub>4</sub>.

**Table 2.** BET Surface Areas of Different Magnetic Nanoparticles

magnetic nanoparticles	BET surface area (m <sup>2</sup> /g)
MnFe <sub>2</sub> O <sub>4</sub>	180.0
MgFe <sub>2</sub> O <sub>4</sub>	70.3
ZnFe <sub>2</sub> O <sub>4</sub>	79.6
CuFe <sub>2</sub> O <sub>4</sub>	93.8
NiFe <sub>2</sub> O <sub>4</sub>	101.2
CoFe <sub>2</sub> O <sub>4</sub>	55.1

of alumina have low cost, high surface area, and good thermal stability.<sup>86–88</sup> These nanoparticles have been used for the removal of cadmium, copper, chromium, lead, and mercury metal ions.<sup>89</sup> The removal efficiencies and characteristics of some metal ions on nanoparticles are discussed below.

**4.1.1. Arsenic.** About 150 million people are drinking arsenic-containing water all over the world due to arsenic groundwater contamination of about 70 countries.<sup>90</sup> Bangladesh is severely affected by arsenic contamination. About 35 million people are drinking arsenic-contaminated water, leading to risk to life.<sup>91,92</sup> This disaster is of a higher magnitude than any seen before in the world. In 1987, the first case of arsenic-induced skin lesions was seen in Bangladesh, but the crisis came to international attention in 1995. A study was conducted in Bangladesh involving the analysis of thousands of water, hair, nail, and urine samples. About 900 villages were reported to have groundwater of higher arsenic concentration than the permissible limit.<sup>93,94</sup> The arsenic contamination problem in this country is still persisting. Several treatment plants have been used in Bangladesh to remove arsenic from the groundwater, but no one is effective at the community scale due to high cost and handling problems.

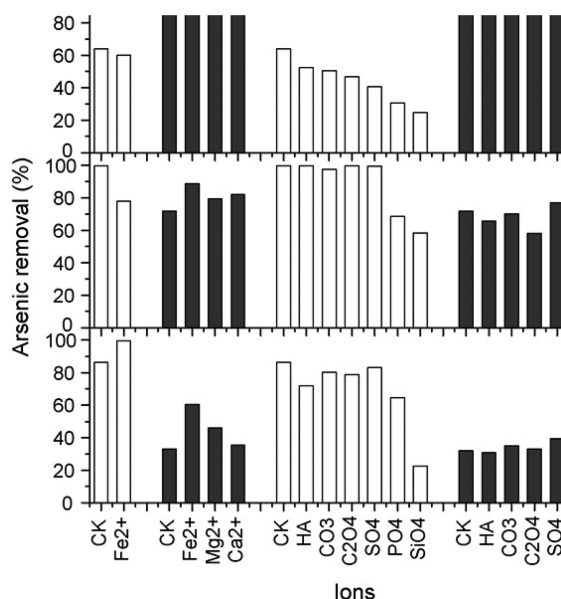
Deliyanni et al.<sup>95</sup> reported 120.0 mg/g as maximum removal of arsenic on a kaganeite ( $\beta$ -FeOOH) nanoparticle. The adsorption data followed the Langmuir adsorption isotherm with endothermic nature. Furthermore, the same group<sup>96</sup> used a nanocrystalline hybrid akaganeite (BET surface area = 231 m<sup>2</sup>/g) for the removal of As(III) from aqueous solutions. The adsorption data fitted well to the Freundlich isotherm. The adsorption followed pseudo-second-order reaction. Pena et al.<sup>97</sup> reported the sorption of As(III) and As(V) on nanocrystalline

titanium dioxide within 60 min. The maximum adsorption reported was 133.0  $\mu$ M/g. The adsorption data fitted well to Freundlich model with pseudo-second-order kinetics. The suitable pH for maximum removal was 7.5–8.0. Kanel et al.<sup>98</sup> reported better adsorption by nanoscale iron in comparison to zerovalent iron. The authors studied the effect of pH, anions, adsorption kinetics, and sorption mechanism. As(V) adsorption was rapid with pseudo-first-order reaction ( $K_{\text{obs}} = 0.02$ – $0.71 \text{ min}^{-1}$ ). The mechanism proposed by laser light scattering analysis was inner-sphere surface complexation. The adsorption interfering anions were carbonic acid, phosphoric acid, and silicic acid. Hristovski et al.<sup>99</sup> discussed As(V) removal on 16 nanoparticles of metal oxides, out of which the most important were TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, and NiO. The removal capacity on all nanoparticles was  $\sim$ 98% except for ZrO<sub>2</sub>. The adsorption data on all nanoparticles followed the Freundlich model well.

Zhu et al.<sup>100</sup> loaded nano zerovalent iron onto activated carbon and used for the adsorption of arsenic pollutant. The adsorption capacity for arsenic was approximately 1.997 mg/g in 2.0 mg/L As(III) solution at pH 6.5. The presence of phosphate and silicate ions decreased arsenic removal, while the effect of other common ions such as sulfate, carbonate, and oxalate was insignificant. The authors claimed this adsorbent as an ideal one for the treatment of arsenic contaminated drinking water. Further, this group<sup>101</sup> prepared a new adsorbent, activated carbon impregnated with nano zerovalent iron, and used for removing arsenate. The adsorption capacity was about 15.4 mg/g at equilibrium concentration of 1.0 mg/L and pH 6.5. The intraparticle diffusion model supported adsorption results. The presence of phosphate and silicate decreased arsenate removal, while the effects of other anions and cations on the arsenic removal were negligible. The authors claimed this method suitable for drinking water treatment due to its good removal capacity. Again, Zhu et al.<sup>102</sup> reported nanosized zerovalent iron, supported onto activated carbon, as an effective adsorbent for arsenic removal from drinking water. The adsorption capacities of arsenite and arsenate, calculated by Langmuir adsorption isotherms, were 18.2 and 12.0 mg/g, respectively. According to the authors, the presence of phosphate and silicate decreased the removal of both arsenite and arsenate, while the effect of other anions and humic acid was insignificant. Besides, calcium and magnesium increased adsorption but ferrous ion decreased this process. The effect of various metal ions on arsenic removal at different pH is shown in Figure 3. A perusal of this figure indicates that the removal efficiency varied with respect to various ions and pHs. At pH 3.0, the most effecting ions were CK, HA, CO<sub>3</sub>, C<sub>2</sub>O<sub>4</sub>, SO<sub>4</sub>, PO<sub>4</sub>, and SiO<sub>4</sub> for As(III). These metal ions effected more As(V) removal at pH 6.5 and 6.9, respectively.

Mostafa et al.<sup>103</sup> described adsorption study of As(V) on to nanosized iron oxide coated quartz (IOCQ). The authors reported 100% arsenic (1000  $\mu$ g/L) removal within 5.0 min. The data followed Langmuir adsorption isotherm. As per the authors, the reported method was suitable for the removal of arsenate from drinking water. Chowdhury and Yanful<sup>104</sup> carried out arsenic removal from aqueous solution on magnetite maghemite nanoparticles. The results showed 96–99% arsenic uptake under controlled pH conditions. The maximum arsenic sorption was 3.69 and 3.71 mg/g for arsenic(III) and arsenic(V), respectively (pH 2.0), with 1.5 mg/L as initial concentration for both species. The authors also described the limitation of arsenic uptake in the presence of a competing anion phosphate. Arsenic uptake decreased with increasing





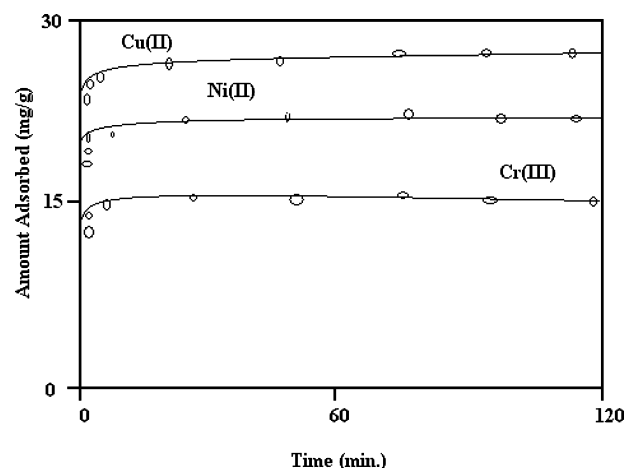
**Figure 3.** Effect of anions on arsenic removal by NZVI/AC at pH 3.5, 6.5 and 9.5. Reprinted with permission from ref 102. Copyright 2009 Elsevier.

phosphate concentration. As per the authors, 60% arsenic uptake was achieved in natural groundwater containing more than 5.0 mg/L phosphate and 1.13 mg/L of arsenic. Jegadeesan et al.<sup>105</sup> reported the sorption of As(III) and As(V) species on nanosized amorphous and crystalline  $\text{TiO}_2$ . The authors prepared amorphous and crystalline nanoparticles with the former as good arsenic removal adsorbent at 4–9 pH range. The isotherms indicated  $\text{TiO}_2$  sorption capacities as dependent on the site density, surface area, and crystalline structure. The adsorbent surface remained almost constant for particles between 5 and 20 nm. But As(V) surface coverage increased with the degree of crystallinity, which had been confirmed by X-ray absorption spectroscopic analysis. The data indicated binuclear bidentate inner sphere complexation of As(III) and As(V) on amorphous  $\text{TiO}_2$  at neutral pH.

**4.1.2. Cadmium.** Cadmium metal ion has been removed from water by using adsorption technology. Skubul et al.<sup>106</sup> reported cadmium removal from water on titanium dioxide nanoparticles modified with thiolacetic acid. The removal of cadmium from aqueous solutions on nanocrystalline akaganeite particle was also reported by Deliyanni et al. and Lazaridis Coworkers.<sup>95,107</sup> Gao et al.<sup>108</sup> described cadmium removal from aqueous solutions on anatase nanoparticle (8–20 nm). The adsorption followed Langmuir isotherm. Furthermore, Deliyanni and Matis<sup>109</sup> evaluated the sorption of cadmium from aqueous solutions on akaganeite nanocrystals. The authors reported chemisorptions with 17.1 mg/g as adsorption capacity. The process was endothermic and adsorption capacity increased from 30 to 90% by increasing temperature 25–65 °C. The adsorption data followed both Langmuir and Freundlich models. Pacheco et al.<sup>110</sup> used alumina silica nanoparticles for the removal of cadmium from wastewater samples. The authors reported 96.4% adsorption on Si–Al particles. These nanoparticles have hydroxyl, alkoxy, and oxy groups, which are responsible for cationic exchange.

**4.1.3. Chromium.** The most common sources of chromium pollution are electroplating, leather tanning, dye, photographic, and cement industries. Ponder and Darab<sup>83</sup> removed

hexavalent chromium by using nanoscale zerovalent iron (10–30 nm diameter). The authors described pseudo-first-order kinetics for the adsorption. Shao-Feng et al.<sup>111</sup> used starch stabilized  $\text{Fe}^0$  nanoparticles as better adsorbent for the removal of Cr(VI) from the groundwater in comparison to native particles. It was observed that the removal of Cr(VI) decreased on increasing pH and nanoparticle dose (0.40 g/L; 100% removal of 20 mg/L). Furthermore, the authors claimed starch stabilized  $\text{Fe}^0$  nanoparticles as better than  $\text{Fe}^0$  powder and filings. Lazaridis et al.<sup>107</sup> achieved 80.0 mg/g removal of Cr(VI) ions at pH 5.5 on nanocrystalline akaganeite adsorbent (3–6 nm diameter with rod-like shape). The data followed Freundlich isotherm well. Hu et al.<sup>112</sup> reported maximum removal of Cr(VI) (19.2 mg/g) from wastewater on maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ , 10 nm diameter) nanoparticles at pH 2.5 and 15 min time. It has also been reported that adsorption was exothermic and controlled by electrostatic interactions and ion exchange phenomenon. Furthermore, these authors<sup>113</sup> used the same nanoparticles for the removal of Cr(VI) from aqueous solutions in the presence of Ni(II) and Cu(II). The authors synthesized these nanoparticles by the sol–gel method with 198  $\text{m}^2/\text{g}$  as BET surface area. The beauty of the method was its short duration of equilibrium time (1.0 min). The adsorption data fitted well to Langmuir model. These authors also described the effect of contact time on adsorption of copper, chromium, and nickel on maghemite nanoparticles (Figure 4). A perusal of this



**Figure 4.** Effect of contact time on adsorption of Cr(VI), Cu(II), and Ni(II) by maghemite nanoparticles. Reprinted with permission from ref 113. Copyright 2006 American Society of Civil Engineers.

figure indicates that the adsorption capacities were in the order of  $\text{Cu(II)} > \text{Ni(II)} > \text{Cr(VI)}$ . Hu et al.<sup>114</sup> studied the removal of chromium on different particle size magnetic nanoparticles. The equilibrium times for these particles were 5–60 min. The different magnetic nanoparticles used were  $\text{MnFe}_2\text{O}_4$ ,  $\text{CoFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$ ,  $\text{NiFe}_2\text{O}_4$ , and  $\text{MgFe}_2\text{O}_4$ . It has been observed that nanoparticle of  $\text{MnFe}_2\text{O}_4$  had the highest adsorption efficiency (99.5%) at pH 2.0. This was due to highest surface area of  $\text{MnFe}_2\text{O}_4$  nanoparticles (180  $\text{m}^2/\text{g}$ ). Cr(VI) removal capacity order was  $\text{MnFe}_2\text{O}_4 > \text{MgFe}_2\text{O}_4 > \text{ZnFe}_2\text{O}_4 > \text{CuFe}_2\text{O}_4 > \text{NiFe}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$ . The adsorption isotherm of chromium removal by various ferrites is shown in Figure 5, which indicates higher adsorption on manganese ferrite. Guan et al.<sup>115</sup> reported adsorption of Cr(VI) metal ion on  $\text{Fe}_3\text{O}_4$ /*Sphaerotilus natans*. The maximum adsorption was 0.0217 mM/g at 3.0 pH. As per the authors, Cr(VI) trapped on

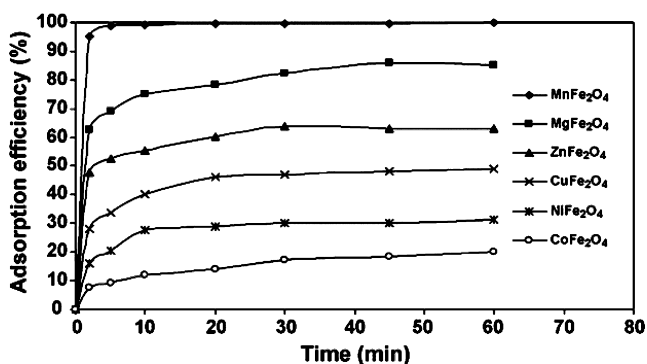


Figure 5. The adsorption isotherm of chromium removal by various ferrite nanoparticles. Reprinted with permission from ref 114. Copyright 2007 Elsevier.

the adsorbent due to  $-\text{CONH}_2$ - and  $-\text{NH}-$  groups of  $\text{Fe}_3\text{O}_4$ /*Sphaerotilus natans* by electrostatic attraction. A comparison of the chromium removal on different nanoparticles and activated carbon is given in Table 3, which clearly indicates the highest adsorption capacity of akaganeite nanocrystals.

Table 3. Comparison of Adsorption Capacities of Different Nanoadsorbents for Cr(VI) Removal

adsorbents	adsorbent capacity (mg/g)	refs
akagancite nanocrystals	80.00	107
carbon nanotube supported ceria nanoparticles	30.20	111
$\delta$ -FeOOH coated maghemite $\gamma$ - $\text{Fe}_2\text{O}_3$ nanoparticles	25.80	178
maghemite nanoparticles	19.20	112
anatase	14.56	233

**4.1.4. Cobalt.** The major sources of cobalt contamination are electroplating, alloys, metallurgical, petrochemical paints, and coal industries. Because of the low toxicity of cobalt, only a few papers are available on the removal of cobalt from aqueous solution by using nanoparticles. Chang et al.<sup>116</sup> used magnetic chitosan nanoparticles for the removal of cobalt from aqueous solutions. The maximum removal (27.5 mg/g) was achieved at pH 3.0–7.0 within 1.0 min. The process was found exothermic, which might be due to low electrostatic interaction between sorbent and nanoparticles at higher temperature. The adsorption data fitted well to Langmuir model. Uheida et al.<sup>117</sup> also reported cobalt removal on nanoparticles of  $\text{Fe}_3\text{O}_4$  and  $\gamma$ - $\text{Fe}_2\text{O}_3$  with  $5.8 \times 10^{-5}$  and  $3.7 \times 10^{-5}$   $\text{Mm}^2$  as maximum loading capacities on the former and later, respectively. The maximum adsorption was achieved within 5.0 min with endothermic nature.

**4.1.5. Copper.** The major sources of copper contamination are waste waters of fertilizer, electrical, metal finishing, paint, electroplating, pigment, and wood manufacturing industries.<sup>95,118–120</sup> Chang and Chen<sup>121</sup> developed monodisperse chitosan bound  $\text{Fe}_3\text{O}_4$  nanoparticles. These were quite efficient for the removal of Cu(II) ions at pH > 2. The adsorption data followed the Langmuir model with maximum adsorption capacity of 21.5 mg/g and equilibrium constant of 0.0165 L/mg. The effects of pH and temperature showed increased adsorption capacity with increasing pH from pH 2–5. The adsorption was exothermic having an enthalpy change of  $-6.14$

$\text{kJ mol}^{-1}$  at 300–330 K. The authors claimed fast removal (in 1 min) because of the absence of internal diffusion resistance. Banerjee and Chen<sup>122</sup> prepared magnetic nanoadsorbent by treating  $\text{Fe}_3\text{O}_4$  nanoparticles with gum arabic. The authors used this adsorbent for the removal of copper metal ion from aqueous solution. Gum arabic was attached to  $\text{Fe}_3\text{O}_4$  via interaction among the carboxylic groups of gum arabic and the surface hydroxyl groups of  $\text{Fe}_3\text{O}_4$ . The equilibrium was achieved within 2.0 min time due to the absence of internal diffusion resistance with increasing pH. The authors compared adsorption of Cu(II) on to the magnetic and the gum arabic modified magnetic nanoparticles. The adsorption capacities were 17.6 and 38.5 mg/g for nonmodified and modified nanoparticles within 2 min. The adsorption data fitted well to Langmuir model. The maximum adsorption of modified nanoparticles was due to carboxylic groups of gum arabic, complexation of the amine group of gum arabic, and surface hydroxyl groups of iron oxide.

Gandhi et al.<sup>123</sup> prepared nanohydroxyapatite (n-HAp) with chitin and chitosan and studied the removal of Cu(II) ions from the aqueous solution. The adsorption capacity of n-HAp, n-HAp/chitin (n-HApC) composite, and n-HAp/chitosan (n-HApCs) composite were 4.7, 5.4, and 6.2 mg/g, respectively, with a contact time of 30 min. The parameters studied were contact time, pH, and selectivity of metal ion. The data fitted well to both Freundlich and Langmuir isotherms. Thermodynamic parameters ( $\Delta G^\circ$ ,  $\Delta H^\circ$ , and  $\Delta S^\circ$ ) were calculated to understand the nature of sorption. The selectivity of the metal ions for the composites was identified along with mechanism. Hao et al.<sup>124</sup> developed magnetic nanoadsorbent (MNP- $\text{NH}_2$ ) by covalent binding of 1,6-hexadamine on the surface of  $\text{Fe}_3\text{O}_4$  and used it for the removal of copper ion from aqueous solution. The different parameters studied were contact time, temperature, pH, salinity, amount of MNP- $\text{NH}_2$ , and initial concentration of copper. The authors evaluated kinetics by Lagergren pseudo-first-order, pseudo-second-order, and Elovich and intraparticle diffusion models. The kinetics followed the pseudo-second-order mechanism, evidencing chemical sorption as the rate-limiting step of sorption. The equilibrium data were analyzed by using Langmuir, Freundlich, and Dubinin–Radushkevich models. The best results were shown by Langmuir isotherm (maximum adsorption capacity of 25.77 mg/g at pH 6 and 298 K; 98% removal). Thermodynamic parameters suggested adsorption spontaneous, endothermic and chemical in nature. Chen et al.<sup>125</sup> synthesized goethite and hematite (nanogoethite and nanohematite) nanoparticles. It was observed that both nanohematite and nanogoethite showed good adsorption capacity for copper ions with maximum adsorption capacity of 149.25 and 84.46 mg/g for nanogoethite and nanohematite, respectively. The experimental data well fitted to Langmuir isotherm and the pseudo-second-order equation.

**4.1.6. Selenium.** The major sources of selenium contamination are agricultural practices, industrial processes such as certain mining, and petrochemical industry, etc. Zhang et al.<sup>126</sup> employed titanium dioxide nanoparticles for the sorption of selenium ions from aqueous solution. The studied parameters were contact time, pH, and temperature. The kinetic data indicated second-order kinetic model ( $k_2 = 0.69$  g/mg  $\text{min}^{-1}$ ) at 293 K. The adsorption process found to be effected by both boundary layer diffusion and intraparticle diffusion. The data followed Langmuir sorption isotherm well. The mean energy of adsorption was calculated by Dubinin–

Radushkevich (D–R) adsorption isotherm at room temperature and found to be  $14.46 \text{ kJ mol}^{-1}$ . The values of  $\Delta H^\circ$  and  $\Delta G^\circ$  indicated exothermic adsorption. Pan et al.<sup>127</sup> prepared a hybrid adsorbent (HFO-201) by irreversibly impregnating hydrated ferric oxide (HFO) nanoparticles for the removal of selenite ( $\text{SeO}_3^{2-}$ ). The adsorbent showed good adsorption selectivity for selenite. The electrostatic interaction from the ammonium groups (bound to D-201 matrix) and the formation of inner-sphere complexes (between the loaded HFO nanoparticles and selenite) were suggested as the adsorption mechanism. Increasing pH and temperature were responsible for decrease of selenite removal on HFO-201. The adsorption data followed Freundlich model well.

**4.1.7. Miscellaneous Metal Ions.** In the above subsections, the removal of a specific metal ion was discussed on a specific nanoparticle, but few papers described the removal of more than one metal ion on a single nanoparticle, which are discussed herein. Zhang et al.<sup>128</sup> developed a polymeric hybrid nanoparticles sorbent (ZrPS-001) and used it for sorption of lead, cadmium, and zinc ions from aqueous solution. The content of heavy metals in treated effluent approached or met the WHO drinking water standard. Afkhami et al.<sup>129</sup> developed 2,4-dinitrophenylhydrazine (DNPH) immobilized on sodium dodecylsulfate coated nanoalumina for the removal of metal cations, i.e., Pb(II), Cd(II), Cr(III), Co(II), Ni(II), and Mn(II), from water samples. The highest adsorption capacity was of Pb(II), Cr(III), and Cd(II) ions. The optimized variables were pH, adsorbent dosage, and contact time. The data fitted well to both Langmuir and Freundlich models. The best fitting of the experimental data was in the Freundlich equation for Mn(II), Pb(II), Cr(III), and Cd(II) ions and the Langmuir model for Ni(II) and Co(II) ions, respectively. Deliyanni et al.<sup>130</sup> reported high removal capacity of zinc ion on akaganeite nanoparticles. The adsorption was exothermic, with 95% as maximum at pH 7.5.

**4.1.18. Anions.** Like metal ions, high concentrations of anions are also not permissible and desirable as these cause some side effects and diseases. The serious side effects of some anions have already been discussed in to the introduction part. The major sources of water contamination by anions are domestic and agriculture activities. In household activities, various commodities are used which release anions to our water resources. Similarly, the application of fertilizers in agriculture and forestry sectors is also responsible for anion contamination of natural water bodies. Besides, the operations of some industries are also responsible for water pollution. Some workers attempted to use nanoparticles for the removal of anions from contaminated water, which are discussed in the following paragraphs.

Sairam et al.<sup>131</sup> used nanohydroxyapatite (n-HAp) particles as an adsorbent for defluoridation with  $1845.0 \text{ mg/kg}$  removal capacity. The authors claimed ion-exchange and adsorption processes as the removal mechanisms. The data fitted well to Langmuir, Freundlich, and Redlich–Peterson isotherms. The thermodynamic parameters were calculated, and the process was found to be controlled by pseudo-second-order and pore diffusion models. The field studies were also carried out for defluoridation in a water sample collected from a nearby fluoride endemic area. Furthermore, the same authors<sup>132</sup> described fluoride removal on nanohydroxyapatite/chitin (n-HApCh) composite. The effects of pH, interfering anions, and contact time were also studied. The adsorption data followed both Langmuir and Freundlich isotherms. The kinetic studies

indicated that the rate of sorption of fluoride on n-HApCh composite followed pseudo-second-order and pore diffusion patterns. It was observed that n-HApCh composite showed higher defluoridation capacity (DC) of  $2840.0 \text{ mg/kg}$  than nanohydroxyapatite (n-HAp). The authors also carried out field trials with the samples collected from a nearby fluoride endemic area.

Bhatnagar et al.<sup>133</sup> evaluated the feasibility of nanoalumina for nitrate removal from aqueous solutions. The parameters optimized were contact time, initial concentration, temperature, pH, and the presence of other interfering anions. The adsorption followed Langmuir and pseudo-second-order kinetic models. The maximum sorption capacity of nanoalumina for nitrate removal was  $4.0 \text{ mg/g}$ . Kassae et al.<sup>134</sup> evaluated zerovalent iron nanoparticles (FeNPs) for the removal of nitrate from water. Martin et al.<sup>135</sup> developed hydrated ferric oxide nanoparticles dispersed within the pore structures of polymeric anion exchanger beads. The results showed high capacity for removing phosphate from water. Xi et al.<sup>136</sup> studied the removal of sulfide from wastewater by nanoscale iron. The adsorption isotherm, kinetics, and mechanism were described. The removal efficiency increased with increasing iron dosage and decreases initial concentration and pH. The removal efficiency was 99.9% at initial concentration of less than  $100 \text{ mg/L}$ . A temperature of  $25^\circ\text{C}$  showed the maximum adsorption of  $19.17 \text{ mg/g}$ . On the other hand, the adsorption capacity decreased at higher or lower temperature. The adsorption data fitted well to both Langmuir and Freundlich models. The sulfide adsorption followed the pseudo-second-order equation with the maximum initial sorption rate. The mechanism of sulfide removal was formation of surface complexes onto the iron nanoparticles via FeOSH and iron sulfides ( $\text{FeS}$ ,  $\text{FeS}_2$ ,  $\text{FeSn}$ ). Huang and Chen<sup>137</sup> developed magnetic nanoadsorbent by covalent binding of poly(acrylic acid) (PAA) on the surface of  $\text{Fe}_3\text{O}_4$  nanoparticles, followed by amino functionalization. It was carried out by using diethylenetriamine (DETA) via carbodiimide activation. The authors reported efficient removal of some anions on the prepared nanoadsorbent.

## 4.2. Removal of Organic Pollutants

Organic pollutants have been removed from water by adsorption technology using nanoparticles. The nanoparticles of aluminum, iron, and titanium oxides and native iron metals are effective for the removal of normal and halogenated hydrocarbons. The removal efficacies of these pollutants are discussed below.

**4.2.1. Dyes.** The major sources of dyes pollution are industries such as textile, paper, rubber, plastics, paints, printing, and leather, etc., which cause pollution in receiving water bodies. The removal of dyes on nanoadsorbents is discussed herein. Belessi et al.<sup>138</sup> synthesized  $\text{TiO}_2$  nanoparticles and used for the removal of reactive red 195 azo dye. The effects of pH, concentration of dye, and adsorbent dose have been studied on the removal of dye. The equilibrium data fitted well to Langmuir and pseudo-second-order kinetic models. At pH 3.0 and  $30^\circ\text{C}$ , the maximum adsorption capacity was  $87.0 \text{ mg/g}$ . The kinetic studies indicated a rapid sorption of dye in the first 30 min with equilibrium at 1 h. Moussavi and Mahmoudi<sup>139</sup> synthesized nanoparticles of  $\text{MgO}$  ( $38\text{--}44 \text{ nm}$  with surface area  $153.7 \text{ m}^2/\text{g}$ ) and used for the removal of azo and anthraquinone reactive dyes from industrial wastewaters. The percentage removal of blue 19 and reactive



red 198 was about 98% at 0.2 g dose, pH 8.0, 50–300 mg/L conc and 5.0 min contact time. The experimental data fitted well to Langmuir and pseudo-second-order rate models. The maximum predicted adsorption capacities were 166.7 and 123.5 mg/g for RB 19 and RR 198, respectively. Chen et al.<sup>140</sup> prepared templated cross-linked chitosan, ECH-RB5, and ECH-3R nanoparticles for removal of azo dyes from aqueous solution. The adsorption was controlled by the initial pH, dye concentration, and temperature. The adsorption process was spontaneous and exothermic with data fitting well in the Langmuir isotherm. The energy of activation calculated by Dubinin–Radushkevich model indicated an adsorption process of a physicochemical nature with predominant adsorption by chemisorption phenomenon. Chang and Chen<sup>141</sup> reported carboxymethylated chitosan conjugated  $\text{Fe}_3\text{O}_4$  nanoparticles for the removal of acid dyes, i.e., orange G and acid green. The adsorption capacity decreased on increasing pH and ionic strength. The adsorption data followed well the Langmuir and pseudo-second-order kinetic models. The adsorption capacities were 1883 and 1471 mg/g for orange G and acid green dyes, respectively. Cheung and Szeto<sup>142</sup> studied the adsorption of acid dye on chitosan nanoparticle. The data fitted well to the Langmuir equation and adsorption capacities were 1.54, 2.66, 1.11, 1.25, and 1.03 mM/g chitosan for orange 10, acid orange 12, acid red 18, acid red 73, and acid green 25, respectively. The adsorption mechanism was predominantly intraparticle diffusion, but there was also a dependence on pore size as the dyes diffuse through macropore, mesopore, and micropore, respectively.

Wang and Wang<sup>143</sup> synthesized a series of biopolymer chitosan/montmorillonite (CTS/MMT) nanocomposites and used them for the removal of congo red. The authors studied the effect of CTS/MMT, conc, pH, and temperature on adsorption process. The results indicated that the adsorption capacity of CTS/MMT nanocomposite was higher than the mean values of CTS and MMT. The sorption process was better fitted by pseudo-second-order equation and Langmuir equation. Du et al.<sup>144</sup> prepared chitosan nanoparticles for adsorption of eosin Y dye from aqueous solution. As per the authors, adsorption of eosin Y on chitosan nanoparticles was affected by contact time, eosin Y concentration, pH, and temperature. The adsorption data followed Langmuir model, and the adsorption capacity was found to be 3.333 mg/g. The adsorption process was endothermic, with 16.7 kJ/mol as enthalpy change at 20–50 °C. Zhao et al.<sup>145</sup> reported the adsorption of methylene blue in aqueous solution onto the silica nanosheets derived from vermiculite via acid leaching. The effect of contact time, initial dye concentration, pH, and temperature was studied. It was observed that increasing dye concentration favored the adsorption, while by increasing pH and temperature, the adsorption decreased. The experimental data fitted well to pseudo-second-order kinetic model. The activation energy, Gibbs free energy, enthalpy, and entropy were 3.42, 65.95, and 0.984 kJ/mol and  $-0.222$  kJ/Kmol at 20 °C, respectively. Sandoval et al.<sup>146</sup> investigated the effects of in situ  $\text{ZrO}_2$  nanoparticle formation on properties of granulated activated carbon (GAC) and used for the removal of methylene blue from aqueous solution. Iram et al.<sup>147</sup> prepared  $\text{Fe}_3\text{O}_4$  hollow nanospheres and tested for the removal of dye contaminants from water. The variation was carried out in initial dye concentration, pH, and contact time for achieving maximum adsorption. The data fitted well to Langmuir and Freundlich adsorption isotherms. The monolayer adsorption

capacity of magnetic hollow spheres (0.05 g) was 105 mg/g. Thermodynamic study showed that the adsorption process was spontaneous and endothermic. The authors described magnetic properties of  $\text{Fe}_3\text{O}_4$  nanospheres useful for dealing environmental pollution.

**4.2.2. Pesticides.** The major sources of pesticide pollution are industries, agricultural, forestry, and domestic activities. However, the pesticides pollution through air has also been reported. The dust particles in air get adsorbed the pesticides (due to pesticides spray in agriculture, forestry, and domestic use) and then contaminate water bodies, sediments, and soil through rainwater,<sup>148</sup> but not much work has been carried out on pesticide removal using nanoparticles. Only one research paper is available in the literature on pesticide adsorption from water. Li et al.<sup>149</sup> reported adsorption of atrazine onto nano- $\text{SiO}_2$  and nanokaolin particles. The influences of ionic strength, atrazine concentration, and pH were studied. The adsorption of atrazine onto nano- $\text{SiO}_2$  and nanokaolin particles decreased with increase of ionic strength. The adsorption data fitted well to Freundlich model.  $K_f$  decreased from 71.55 to 37.22 by varying dose of nanokaolin from 5.0 to 20.0 g/L. It was interesting to observe that adsorption decreased on both nanoparticles by increasing pH, which suggested the speciation change of atrazine as the dominant factor for adsorption phenomenon.

**4.2.3. Hydrocarbons.** The most common sources of hydrocarbons are dry cleaning solutions, paint, spot remover, rubber cement, solvents, and other industries with a major contribution from the petrochemical industry. Yang and Xing<sup>150</sup> reported adsorption of phenanthrene on nano- $\text{TiO}_2$  and ZnO particles. The authors varied various experimental conditions and reported maximum adsorption. Furthermore, this group<sup>151</sup> described adsorption of phenanthrene by nano- $\text{Al}_2\text{O}_3$  particles coated with humic acid. As in the case of previous work, the adsorption was optimized by various experimental variables.

### 4.3. Removal of Biological Pollutants

The major sources of biological contamination are domestic activities. Sometimes, agriculture processes also participate in biological water contamination. Attempts have been made to search the literature for the removal of biological pollutants by adsorption on nanoparticles. Only a few papers are available on this.

**4.3.1. Viruses and Bacteria.** Virus and bacteria are the most notorious pathogens for human beings. They cause various types of diseases. Sometimes, these pathogens are lethal and a threat to our lives. Water contamination due to these pathogens is a usual phenomenon. Nanoparticles have also been used by some workers to remove these sorts of contaminants from water. Shen et al.<sup>152</sup> reported adsorption of virus on four varieties of iron oxide nanoparticles, with 100% adsorption on  $\alpha\text{-Fe}_2\text{O}_3$  nanoparticles. The adsorption percentage increased with decreasing virus initial concentration. The virus adsorption was found to be reduced in high ionic strength of the background solution, indicating electrostatic interaction as controlling parameter. The adsorption data fitted well to both Langmuir and Freundlich models. The estimated adsorption parameters indicated the presence of multilayer and favorable adsorption. Anions like  $\text{HPO}_4^{2-}$  and  $\text{HCO}_3^-$  also reduced virus adsorption, which might be due to competitive adsorption of virus and anions. Li et al.<sup>153</sup> used nanoscale zerovalent iron (NZVI) as a bactericidal for *Escherichia coli*



Table 4. Applications of Nanoparticles for the Removal of Water Pollutants by Adsorption

soln. no.	pollutants	adsorbents (nanoparticles)	removing capacities	contact time	pH	refs
Inorganic Pollutants						
1	As(III)	zero-valent Iron(10–100 nm)	3.5 mg/g	12 h	7	84
2	As(III)	akaganeite (hybrid surfactant)		100 min	7	96
3	As(III)	zero-valent iron onto activated carbon	1.997 mg/g	12 h	6.5	100
4	As(III)	zirconia	1.85 mM/g	48 h	11.0	234
5	As(V) and As(III)	titanium dioxide (6 nm)	As(V) 95 $\mu$ M/g and As(III) 50 $\mu$ M/g	4 h	pH < 8 for As(V), pH > 7.5 for As(III)	97
6	As(V) and As(III)	magnetite Fe <sub>3</sub> O <sub>4</sub> (12 nm)		24 h	4.8–8.0	235
7	As(V)	akaganeite (2.6 nm)	120 mg/g	24 h	7.5	95
8	As(V)	zero-valent iron (30 nm)			3–7	98
9	As(V)	alumina silicate treated with Fe(II)	22.5 mg/g for zeolite, <18 mg/g for clinoptilolite, and 10 mg/g for metakaoline	96 h	5.5	236
10	As(V)	metal-oxide		7 h		99
11	Cd(II)	thiolactic acid modified titanium dioxide (4.5 nm)			pH < 5	106
12	Cd(II)	anatase (8–20 nm)	244.13 $\mu$ M/g for RHT 47, and 497.90 $\mu$ M/g for RHT 69		6.1	108
13	Cd(II)	akaganeite (2.6 nm)	17.1 mg/g		8	109
14	Cd(II)	alumina–silica (32 nm)			6.5	110
15	Co(II)	Fe <sub>3</sub> O <sub>4</sub> and $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (10 nm)		3 min	5 for Fe <sub>3</sub> O <sub>4</sub> , 6 for $\gamma$ -Fe <sub>2</sub> O <sub>3</sub>	118
16	Co(II)	magnetic chitosan (13.5 nm)	27.5 mg/g	1 min	5.5	116
17	Cr(VI)	iron			7	110
18	Cr(VI)	maghemite (10 nm)		15 min	2.5	160
19	Cr(VI)	akaganeite (3–6 nm)	80 mg/g	72 h	5.5	106
20	Cr(VI)	MnFe <sub>2</sub> O <sub>4</sub> (10 nm)	31.5 mg/g	5 min	2	180
21	Cr(VI)	carbon nanotube supported ceria (6 nm)	30.2 mg/g	24 h	3.0–7.4	160
22	Cr(VI)	$\delta$ -FeOOH coated maghemite $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> (15 nm)	25.8 mg/g	30 min	2.5	178
23	Cu(II)	gum arabic modified magnetic (13–67 nm)	38.5 mg/g	2 min	2.0–5.1	122
24	Cu(II)	chitosan-bound Fe <sub>3</sub> O <sub>4</sub> magnetic (13.5 nm)	21.5 mg/g	1 min	5	237
25	Cr(III)	nitrogen-doped magnetic carbon		120 min	8	238
26	Hg(II)	alumina (50 nm)			6.5	239
27	Hg(II)	Fe <sub>3</sub> O <sub>4</sub>	125.0 mg/g	50 min	5.0	240
28	Hg(II)	mercapto-functionalized nano-Fe <sub>3</sub> O <sub>4</sub> magnetic polymers (SH-Fe <sub>3</sub> O <sub>4</sub> -NMPs)		60 min	3.0	241
29	Se(II)	titanium dioxide		5.0 min	2–6	126
30	Zn(II)	akaganeite	27.61 mg/g	20 h	6.5	130
31	Zn(II)	magnetic modified chitosan	32.16 mg/g	30 min		242
32	Cr(VI), Cu(II) and Ni(II)	maghemite (10 nm)		24 h	2.5 for Cu(II), 6.5 for Cu(II), and 8.5 for Ni(II)	113
33	Cr(VI) and Pb(II)	zero-valent (10–30 nm)		5–10 min	6–7	83
34	Cr(VI), Cd(II), Cu(II), Hg(II), and As(VI)	alumina (50 nm)			5.25–6.05	89
Organic Pollutants						
35	red 195 azo	TiO <sub>2</sub>	87.0 mg/g	1 h		138
36	azo and anthraquinone reactive	MgO (38–44 nm)	98%		pH 8.0	139
37	orange G and acid green	Fe <sub>3</sub> O <sub>4</sub>	1883 and 1471 mg/g for orange G and acid green dyes			141
38	acidic metanil yellow and reactive blue 15	cross-linked chitosan	1334 mg/g for metanil yellow and 722 mg/g for dye reactive blue 15		pH 4.0	243
39	eosin Y	chitosan	3.333 mg/g			144
40	methylene blue	ZrO <sub>2</sub>	0.5 mg/g	3 days	7–9	146
41	methylene blue	magnetite nanoparticles coated with an anionic biopolymer poly( $\gamma$ -glutamic acid)	78.67 mg/g		1.0	244
42	methylene blue, neutral red, and methyl orange	Fe <sub>3</sub> O <sub>4</sub>	1–2 mg/g	60 min	6–7	245
43	methylene blue (MB) and cresol red (CR)	Fe <sub>3</sub> O <sub>4</sub>	6–35 mg/g	60 min	6–8	246
44	methylene blue and Congo red	magnetite	70.4 mg/g and 172.4 mg/g for methylene blue and Congo red			247
45	methylene blue	FeTiO <sub>3</sub> and ilmenite	71.9 mg/g			248
46	Congo red	Zn–Fe <sub>2</sub> O <sub>4</sub>	16.58 mg/g		6.0	249

Table 4. continued

soln. no.	pollutants	adsorbents (nanoparticles)	removing capacities	contact time	pH	refs
Organic Pollutants						
47	rhodamine 6 G	hexadecyl functionalized magnetic silica	35.6 mg/G		11.0	250
48	malachite green	halloysite nanotubes	99.6 mg/g	30 min	9.5	251
49	reactive red-120 and 4-(2-pyridylazo) resorcinol	Fe <sub>3</sub> O <sub>4</sub>	166.67 and 49.26 mg/g for both dyes	2.0 min	2.5	252
50	N719 dye	TiO <sub>2</sub>	65.2 (30 °C), 68.2 (40 °C), and 76.6 (50 °C) mg/g			253
51	acid orange 7 and acid orange 10	ethylenediamine-modified magnetic chitosan	3.47 mM/g for AO7 and 2.25 mM/g for AO10		10.0	254
52	phenol	Fe <sub>3</sub> O <sub>4</sub> poly(methylmethacrylate-co-divinylbenzene)		5 min	6–7	255

from groundwater. The authors exposed nanoscale zerovalent nanoparticles for various molecules and tested their bactericidal properties. The exposure to 100 mg/L of NZVI with 28% Fe<sup>0</sup> content resulted into 2.2-log inactivation. Adsorbed poly-(styrene sulfonate) (PSS), poly(aspartate) (PAP), or NOM on NZVI with the same Fe<sup>0</sup> content significantly decreased its toxicity, causing less than 0.2-log inactivation and 1.8-log inactivation observed for NZVI with 7.0% Fe<sup>0</sup>. However, the minimum inhibitory concentration (MIC) after 24 h was 5.0 mg/L regardless of Fe<sup>0</sup> content. The MIC of PSS, PAP, and NOM coated NZVI were 500, 100, and 100 mg/L, respectively, but MIC was much lower than the typical injection concentration used in remediation (10 g/L). Probably, the bactericidal properties of the modified nanoscale zerovalent iron nanoparticles were due to adsorption which check the propagation of *E. coli*. The removal of some important pollutants from aqueous solutions on different adsorbents is summarized in Table 4.

#### 4.4. Applications of Nanotubes

Carbon nanotubes are a special type of nanosized structures which have been used as adsorbents in water treatment due to their high chemical stability and surface area. The adsorption of various metal ions on this adsorbent has been carried out by some workers, which resulted into publications more than any type of nano-adsorbent. Therefore, attempts have been made to discuss the removal of metal ions on nanotubes in this separate subsection. Carbon nanotubes are of single-walled carbon nanotubes (SWCNT) and multiwalled carbon nanotubes (MWCNT). The structures of these two types of carbon nanotubes are shown in Figure 6. Some important paper describing the removal of different metal ions from water are discussed herein.

Li et al.<sup>154</sup> reported the removal of Cd(II) from aqueous solution on surface oxidized carbon nanotubes with H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>, and HNO<sub>3</sub>. The oxidation of carbon nanotubes resulted into more hydrophilic surface along with enhancement of oxygen containing functional groups such as carboxylic, phenolic, and lactone. These groups have increased ion exchange capacity of carbon nanotubes.<sup>155</sup> The experimental results suggested that cadmium(II) adsorption capacities for three kinds of oxidized CNTs increased due to the functional groups introduced by oxidation. Cadmium(II) adsorption capacity of CNTs was 1.1 mg/g, which reached to 2.6, 5.1, and 11.0 mg/g for H<sub>2</sub>O<sub>2</sub>, KMnO<sub>4</sub>, and HNO<sub>3</sub> oxidized CNTs, respectively. According to the authors, the adsorption was strongly pH dependent and increased for KMnO<sub>4</sub> and HNO<sub>3</sub> treated CNTs. Li et al.<sup>156</sup> also studied the adsorption thermodynamics and kinetics of Pb(II) removal by adsorption

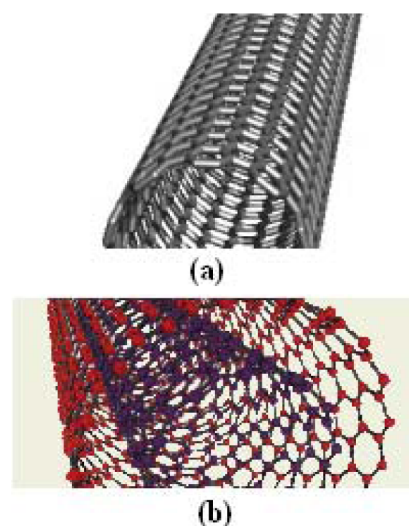
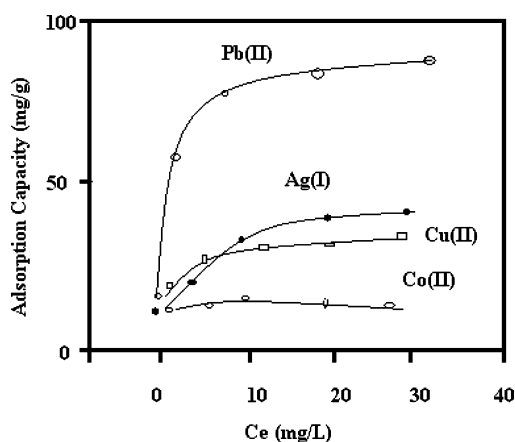


Figure 6. The structures of (a) SWCNT and (b) MWCNT.

on CNTs. The adsorption was endothermic and the data fitted well to Freundlich and pseudo-second-order rate models. Kochkar et al.<sup>157</sup> used MWCNTs for the removal of Cd(II), Pb(II), and Cu(II) ions from aqueous solutions. The adsorption data obeyed the Langmuir model, and adsorption capacities were found to be 97.08, 24.49, and 10.86 mg/g for Pb(II), Cu(II), and Cd(II), respectively. Yang<sup>158</sup> used Stone–Wales defect sites in zigzag and armchair single-walled carbon nanotubes for nickel adsorption. The authors studied the effect of the Stone–Wales defect on adsorption phenomenon. It was determined that the sites formed by fusions of 7–7 and 6–7 rings were the most exothermic in the cases of (10,0) and (5,5) defective tubes. Besides, carbon–carbon bonds associated with Stone–Wales defects were more reactive than a perfect hexagon, increasing nickel adsorption. Nickel adsorption showed a relationship to the orientation of the Stone–Wales defects with respect to the tube axis. Zinc metal ion was removed from water on commercial single-walled and multi-walled CNTs by Lu and Chiu.<sup>159</sup> The equilibrium time was 60 min, and the removal increased from 1.0 to 8.0 pH. The adsorption capacity for Zn(II) was 43.66 mg/g for SWCNTs and 32.68 mg/g for MWCNTs. Di et al.<sup>160</sup> developed an aligned carbon nanotube and used it for the removal of chromium from drinking water. The adsorption capacity reported was 30.2 mg/g at pH 7.0, 1.5 times higher than activated carbon. Doong and Chiang<sup>161</sup> synthesized carbon nanotubes (CNT) and titanate nanotubes (TNT) and used them for adsorption of copper metal ion. The data fitted well to

the Langmuir model, giving adsorption capacities in the range of 83–124 mg/g for copper and 192–588 mg/g for lead metal ions.

Stafiej and Pyrzynska<sup>162</sup> reported adsorption of Cu(II), Co(II), Mn(II), Pb(II), and Zn(II) metal ions on CNTs (5–10 nm; 40–600 m<sup>2</sup>/g surface). The order of removal was Cu(II) > Pb(II) > Co(II) > Zn(II) > Mn(II) at pH 9.0. The adsorption data fitted well to Freundlich adsorption isotherm. Wang et al.<sup>163</sup> reported the adsorption of lead, silver, copper, and cobalt metal ions on acidified multiwalled carbon nanotubes. The equilibrium time of adsorption was 5.0–20.0 min (Figure 7).



**Figure 7.** Adsorption isotherm of acidified MWCNT for removal of lead, silver, copper, and cobalt metal ions. Reprinted with permission from ref 163. Copyright 2007 Elsevier.

The adsorption mechanism proposed was due to the presence of oxyfunctional groups on acidified MWCNTs. Wu<sup>164</sup> studied the removal of Cu(II) on to HNO<sub>3</sub> and NaOCl modified CNTs. The adsorption capacities of Cu(II) increased by changing pH from acidic to basic range. The adsorption data fitted well to the Langmuir model.

Lou et al.<sup>165</sup> used single-walled carbon nanotubes for the removal of dissolved organic matter (DOM) in raw water. The authors optimized pH, ionic strength, and temperature as controlling parameters. The adsorption capacity of SWCNTs increased with increasing DOM concentration and decreased with an enhancing ionic strength. The equilibrium was attained after 120 min. The modified Freundlich model was used to treat the data. The adsorption was of pseudo-first-order. The adsorption process was controlled by pore diffusion that was confirmed by the fits of the intraparticle diffusion model. The maximum adsorption capacities were 26.1–20.8 mg/g at 4 and 45 °C. Machado and co-workers<sup>166</sup> removed reactive red M-2BE textile dye from aqueous solutions on multiwalled carbon nanotube. The effects of pH, shaking time, and temperature were studied. In the acidic pH (pH 2.0), the adsorption of the dye was favorable. The contact time to obtain equilibrium was 1 h. Avrami fractional-order kinetic model provided the best fit of the data. Shim and co-workers<sup>167</sup> described the removal of benzene, toluene, and *m*-xylene on thin multiwalled carbon nanotubes (t-MWCNTs). The adsorption data of these compounds were calculated. The temperature-dependent Toth isotherm model was employed to correlate the experimental adsorption isotherm data. The isosteric heat of adsorption was calculated from van't Hoff equation. The results suggested a quite satisfactory removal of these hydrocarbons from water. The adsorption capacity and surface area of some

CNTs used for removal of metal ions are given in Table 5. A perusal of this table indicates sufficient adsorption capacities of

**Table 5.** Adsorption Capacities and Surface Area of CNTs

CNTs (m <sup>2</sup> /g)	adsorption capacity (mg/g)	surface area
as grown	1.10	82.20
H <sub>2</sub> O <sub>2</sub> oxidized	2.60	130.0
HNO <sub>3</sub> oxidized	5.10	84.30
KMnO <sub>4</sub> oxidized	11.00	128.0
NaOCl oxidized	47.40	94.90

carbon nanotubes for different pollutants. It is important to mention here that CNTs have certain limitations in water treatment by the adsorption method. Sometimes, CNTs coagulated in water lose nano identity. The coagulation of CNTs depends on the water quality. The presence of organic matter and algae are responsible for CNTs coagulation. The doses of CNTs are also control the coagulation of CNTs. Therefore, these points can be considered as the limitations of CNTs in water treatment. Therefore, a suitable dose of CNT is used for water treatment with no organic matter and algae.

## 5. SEPARATION OF NANOPARTICLES

The removal of nanoparticles after adsorption is a little bit of a tedious job due to their small size, and health and environmental issues. The separation of nanoparticles from aqueous solution needs expertise hands with careful handling. Basically, the separation of nanoparticle from aqueous solution depends on their nature. The different methods have been used for separating nanoparticles from aqueous solution and the most important include magnetism, cross-flow filtration, and centrifugation. Generally, magnetic nanoparticles contain magnetic elements such as iron, nickel, and cobalt. These types of nanoparticles can be separated from water easily by high gradient magnetic separation (HGMS). HGMS has been applied to more complex separations via the use of functionalized magnetic particles, which are tailored to selectively remove the environmental pollutants. In HGMS, the separation of nanoparticles depends on magnetic field gradients, magnetic properties, and sizes of the nanoparticles.<sup>168</sup> The most commonly separated nanoparticle by HGMS are iron oxide, maghemite, maghemite, chitosan coated magnetic, gum arabic modified, magnetic chitosan, etc. The cross-flow membrane filtration has been used to separate nanoparticles in many applications like chemical, biological, and environmental.<sup>169</sup> Nanoparticle transport in cross-flow membrane filtration is controlled by Brownian diffusion, permeate convection, and electrokinetic migration. Besides, gravitational settling, shear induced diffusion, axial convection and inertial lift also contribute at small level.<sup>170</sup> This technique depends on the size and the type of the membrane used. The selectivity of the membrane depends on the size of nanoparticles to be separated. In the literature, the commonly separated nanoparticles from water are FeO, aligned carbon nanotubes, akaganeite, nanocrystalline hybrid, akaganeite, surfactant-akaganeite, etc.

The centrifugation separation of nanoparticles has been proven to be a more effective method due to its high efficiency, capability of scalable production, and free of nanoparticle aggregation.<sup>171–173</sup> The velocity related rate zonal and density based isopycnic centrifugations have been reported. The isopycnic centrifugation is better for the separation of small



size (less than 10.0 nm) nanoparticles due to the conversion of overall density (after salvation) into the density range of gradient medium. Contrarily, larger size nanoparticles (larger than 10.0 nm) are denser than water and, hence, are separated by the velocity related rate zonal centrifugation.<sup>174–176</sup> Generally, the speeds of centrifuge machine are 20000–50000 rpm magnitude, capable of removing nanoparticles from water. The commonly separated nanoparticles from water by this method are  $\text{Fe}_3\text{O}_4$ ,  $\text{Fe}_2\text{O}_3$  and  $\gamma\text{-Fe}_2\text{O}_3$ , zerovalent iron kaolinite-supported zerovalent iron, gellan gel, etc. A survey of various separating methods for nanoparticles is given in Table 6. This table indicates that external magnetic field and membrane filtration methods have been used frequently for the removal of nanoparticles from aqueous solution.

**Table 6. The Different Separation Methods from Water for Nanoparticles**

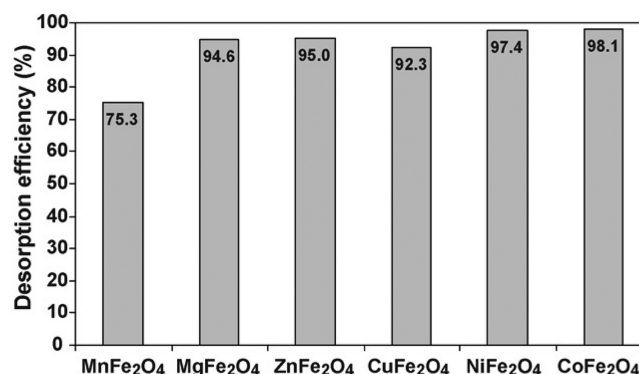
methods	nanoparticles	refs
external magnetic field	maghemite	112
	maghemite	256
	chitosan coated magnetic	257
	gum arabic modified	122
	$\text{Fe}_3\text{O}_4$	177
	magnetic chitosan	117
cross-flow filtration	FeO	111
	aligned carbon nanotubes	160
	akaganeite	95
	nanocrystalline hybrid	96
	surfactant–akaganeite	
	akaganeite	109
centrifugation	$\text{Fe}_3\text{O}_4$	235
	zero valent iron	258
	$\text{Fe}_3\text{O}_4$ and $\gamma\text{-Fe}_2\text{O}_3$	117
	kaolinite-supported zerovalent iron	259
	gellan gel	260

## 6. REGENERATION OF NANOPARTICLES

Regeneration of adsorbents in water treatment is one of the crucial aspects as it controls the economy of water treatment technology. My experimental experience and observation dictate to me that pH dependent solvents play crucial roles in regeneration of adsorbents. Some workers attempted to regenerate nanoparticles for recycling. A few important studies dealing this issue are discussed herein.

Uheida et al.<sup>177</sup> studied the regeneration of  $\text{Fe}_3\text{O}_4$  nanoparticles after adsorption of Pd(II), Pt(IV), and Rh(III). The regeneration reagents used were perchlorate, sodium bisulfate solution, and nitric acid. The authors reported successful regeneration of nanoparticles and observed desorption as pH dependent. Furthermore, the same group<sup>117</sup> reported desorption of Co(II) from  $\text{Fe}_3\text{O}_4$  and  $\gamma\text{-Fe}_2\text{O}_3$  nanoparticles. The percentage recoveries of cobalt was 86 and 30 from  $\gamma\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  nanoparticles, respectively. This difference in recoveries might be due to ion exchange between Co(II) and Fe(II) metal ions. Hu et al.<sup>178</sup> reported regeneration of  $\gamma\text{-Fe}_2\text{O}_3$  coated with  $\delta\text{-FeOOH}$  nanoparticles by desorption of Cr(VI). Ninety-Eight percent of Cr(VI) was recovered by using 0.01 M NaOH, with no change in adsorption capacity. Guan et al.<sup>110</sup> reported 90% desorption of  $\text{Fe}_3\text{O}_4$ /*Sphaerotilus natans* by HCl.

Mostafa et al.<sup>103</sup> regenerated nanosized iron-oxide-coated quartz (IOCQ) by using HCl. The authors regenerated the adsorbent for further removal of arsenic successfully. Namdeo and Bajpai<sup>179</sup> described Cr(VI) desorption from magnetite nanoparticles by using KCl solution of different molarity. Hu et al.<sup>180</sup> described suitability of 0.01 M NaOH for the desorption of Cr(VI) from Jacobsite nanoparticle, with 98.9% as desorption efficiency. The authors claimed good efficiency of this adsorbent after six cycles of adsorption/desorption processes. Furthermore, the same authors<sup>113</sup> reported remarkable study of Cr(VI), Cu(II), and Ni(II) desorption from magnetite nanoparticles. As per the authors, there was no significant difference in the capacity of maghemite after five successive adsorption/desorption cycles. The same authors<sup>114</sup> reported regeneration of various ferrite nanoparticles after removal of chromium metal ions. The regeneration was achieved by 0.10 M NaOH solution. The desorption efficiencies of different ferrites nanoparticles are shown in Figure 8, which indicates maximum desorption from cobalt



**Figure 8.** The different desorption efficiency of chromium adsorbed ferrites. Reprinted with permission from ref 114. Copyright 2007 Elsevier.

ferrite. Deliyanni et al.<sup>95</sup> reported 25–30% loss in adsorption capacity after each desorption process of As(V) from akaganeite nanocrystals. After maximum desorption cycles, only 75% of metal could be recovered. Banerjee and Chen<sup>122</sup> used hydrochloric acid of different pHs for regeneration of arabic nano-adsorbent after removal of copper. It was observed that pH 1.5 resulted into 93% desorption. Higher efficiency at lower pH might be due to the presence of high amounts of hydrogen ions. The regeneration of copper metal was 28.12, 27.64, and 27.18 mg/g after first, second, and third adsorption/desorption processes, respectively. Zhu et al.<sup>100–102</sup> got desorbed arsenic from zerovalent iron onto activated carbon and activated carbon impregnated with nano zerovalent iron adsorbents by using 0.1 M NaOH solution. Zhang et al.<sup>126</sup> employed 0.1 M NaOH for regenerating titanium dioxide nanoparticles for further uptake of selenium ions from aqueous solution. Zhang<sup>128</sup> described the regeneration of polymeric hybrid nanoparticles sorbent (ZrPS-001) with 6.0 M HCl solution for repeated use without any significant capacity loss. Afkhami et al.<sup>129</sup> evaluated three adsorption/desorption cycles for 2,4-dinitrophenylhydrazine (DNPH) immobilized on sodium dodecylsulfate-coated nanoalumina by desorption of cadmium and zinc ions by using a mixture of nitric acid and methanol. Chen et al.<sup>140</sup> regenerated templated cross-linked chitosan, ECH-RB5, and ECH-3R nanoparticles by the alkaline solution of azo dye adsorption. Pan et al.<sup>127</sup> regenerated HFO-201 by

using a binary NaOH–NaCl solution after removal of selenite. Martin et al.<sup>135</sup> regenerated hydrated ferric oxide nanoparticles after removal of phosphate. The regeneration was achieved by 4% NaOH and 2% NaCl solutions. About 80% phosphorus was eluted in the first cycle. As per the authors, there was no loss of performance after 10 regeneration cycles, and levels of eluted phosphate were consistently high. These results suggested that the media has high potential for the recovery of phosphate. These results indicated that nanoparticles could be regenerated and used for water treatment, which made these particles as economic tools. This property of nanoparticles may be considered as an extra advantage for their popularity in wastewater treatment.

The management of the used nanoparticles and recovered pollutants is one of the most important aspects. It has been observed that there is no paper describing the management of the recovered pollutants and exhausted nanoparticles. However, everybody is aware about pollutant hazards and nanotoxicology, and it can be assumed that the proper disposal could have been carried out by the users. The best way of disposal management is recycling of nanoparticles. The used and exhausted nanoparticles may be used in the manufacturing of bricks, stones etc. Besides, their disposal may be carried out by filling them in steel cylinders and dumping them deep into the earth. The regenerated metal ions may be recycled for manufacturing various commodities. On the other hand, the recovered organic contaminants should be treated as the priority pollutants. These should be filled in steel cylinders and dumped deep into the earth.

## 7. NANOTOXICOLOGY

Nanotoxicology describes the toxicity of nanoparticles (<100 nm diameter). It deals with the threat extended to the environment and human beings. The small size of nanoparticles makes their entry easy into the living systems. The mostly studied nanoparticles for toxicity are of titanium dioxide, alumina, zinc oxide, carbon black, and carbon nanotubes. Nanoparticles have larger surface area to unit mass ratios, surface charge, and aggregation, which may lead to pro-inflammatory effects (mostly lung tissue). Besides, some nanoparticles may be able to translocate from one site to another and affect vital organs of human body such as blood, liver, skin, gut, and brain. The most common entry of nanoparticles into our body is through skin,<sup>181</sup> inhalation,<sup>182</sup> ingestion,<sup>183</sup> etc. After getting entry into the bloodstream, they can reach to various body parts such as brain, heart, liver, kidneys, spleen, bone marrow, and nervous system.<sup>184–187</sup>

The toxicities of nanoparticles are because of their shape, size, and greater surface area to volume ratio. This property leads to high chemical reactivity and biological activity, which results into greater chemical reactivity and production of reactive oxygen species (ROS). The generation of ROS has been reported as the property of carbon fullerenes, carbon nanotubes, and nanoparticle metal oxides. The production of ROS and free radicals is one of the primary mechanisms of nanoparticle toxicity. The presence of ROS and free radicals may cause oxidative stress, inflammation, and consequent damage to proteins, membranes, and DNA.<sup>188</sup> Besides, some nanoparticles overload the body's phagocytes and trigger stress reactions, which lead to inflammation and weaken the body's immune system. Some nonbiodegradable particles get absorbed on the surface of our body macromolecules and affect regulatory mechanisms of enzymes and other proteins. Some

studies also demonstrated that nanoparticles may cause DNA mutation,<sup>187</sup> major structural damage to mitochondria, and cell death.<sup>185,189</sup> Agglomeration is the phenomenon by which nanoparticles show toxicities in the environment.<sup>190</sup> Some reviews<sup>191–199</sup> have been appeared on nanotoxicology. These articles described various aspects of nanotoxicology such as sources, cytotoxicities, public health concerns, predictive models, awareness, regulatory perspective, etc.

It is interesting to note that the behavior of nanoparticles inside the body is still a major question that needs to be addressed. The difficulty in assessing nanotoxicology is the characterization of nanoscale contaminants. The biological systems at the nanoscale are still not known exactly. Because of these hurdles, it is not possible to determine exactly the toxicities of nanoparticles in our earth's ecosystem.<sup>200</sup> Although electron microscopy (SEM and TEM) and atomic force microscopy (AFM) techniques are good tools to assess the nanostructural world, nanotoxicology still requires extremely precise determination of biological systems and contaminants at nano levels. Nanotoxicology is a fantastic and emerging area, which needs more concentration of scientists toward exploring the complete toxicities of the nanoparticles.

At the moment, there are no specific guidelines to deal with the nanotoxicities. However, Schmidt-Ott et al.<sup>201</sup> discussed some points for consideration as safety measures. Similarly, a report on health based occupational exposure limit exists for nanomaterials. It was submitted by the National Institute for Public Health and the Environment (RIVM).<sup>202</sup> Besides, WK8985, *Guide for Handling Unbound Engineered Nanoparticles in Occupational Settings*,<sup>203</sup> also describes the health standards. Basically, the nanotoxicity is due to inhalation and skin contact of nanoparticles. The nanotoxicity can be minimizing by the following precautions:

- (1) Eliminate: Do not allow others (guest, visitors etc.) to enter a place of nanotechnology.
- (2) Isolate: Use closed systems when working with nanomaterials.
- (3) Ventilate: Always work in a fume hood or a ventilated area.
- (4) Protection: Always wear respiration protection and gloves when working.
- (5) Transportation: Dispose of and transport nanowastes as per the guidelines of hazardous chemical wastes, i.e., in closed containers.
- (6) Management: Do not spread nanowastes in the open.
- (7) Pyrophoricity: Always test nanopyrophoricity before introducing nanomaterials to the public.

## 8. FUTURE PERSPECTIVES OF NANOPARTICLES

In spite of the bright future of nanoparticles in water treatment, there are some issues related to safety profiles as discussed above. Nanoparticles are the new identities to the environment and may become a serious issue in the near future. Some of them are nonbiodegradable and enter into the human body.<sup>204,205</sup> Presently, there is no nanoparticle that is completely safe and nontoxic. The probability of environmental contamination is their release during synthesis, application, and disposal management. The most probable affected environmental regimes are water, soil, and air through which they can enter into the body of human beings and other animals. Besides, plants can also absorb nanoparticles from water and soil and accumulate into their edible parts. Therefore, there is a

great need to develop safe and suitable strategies for their disposal. Taking this issue seriously, The U.S. Environmental Protection Agency funded a research project in 2003 to study the adverse effect of nanoparticles on the environment.<sup>206</sup> Eco-friendly nanoparticles may be prepared by considering their environmental sustainability and biodegradability. The improvement in nanoparticles may be achieved by tuning their size and shape. The required nanoparticles may be prepared by optimizing formulation steps, sterilization, and storage. There is a need to develop more efficient, selective, inexpensive, and eco-friendly nanoparticles to play a key role in future water treatment. The characteristics shown by these materials may help scientists to come up with more ideas on how to produce cleaner water. There is a great need to test genotoxicity and cytotoxicity through *in vivo* toxicity models before launching these materials at a community level. Besides, the transformation of pollutants into more toxic products is also an important issue. We should also develop such water treatment methods which can take care of them too.

The safety issue and the working capabilities of nanoparticles are also important for determining their future. A comparison of nanoparticles with low cost adsorbents was carried out for assessing their future perspectives. It is interesting to note that there is no paper describing pilot and commercial scale applications of nanoparticles. In addition to this, the regeneration of nanoparticles is still in the development stage. Besides, the management of the exhausted nanoparticle is not completely developed. Therefore, it is not possible to compare the working capabilities of nanoparticles with low cost adsorbents. However, efforts were made to compare nanoparticles with low cost adsorbents (conventional adsorbents). Ali et al.<sup>55,207</sup> reviewed the applications of low cost adsorbents for the removal of organic and inorganic pollutants from water. The data of these reviews was compared with those mentioned in this article. It was observed that the exact comparison is not possible due to varied experimental conditions used in the case of low cost and nanoparticles adsorbents for the removal of same pollutant. However, efforts were made to compare these two types of adsorbents for a variety of pollutants. Low cost adsorbents have been used for the removal of almost all kinds of pollutants, i.e., inorganic, organic, and biological origins. Contrarily, nanoparticles have been used for removing a few contaminants only. Of course, low cost adsorbents are inexpensive in comparison to nanoparticles, but nanoparticles may be inexpensive in the near future by optimizing their preparation at an industrial scale.

It was observed that nanoparticles seem to be better adsorbents. It is due to their good working capacities. A general trend was observed during comparison of nanoparticles with low cost adsorbents. In most of the cases, the contact time for nanoparticles was low (1.0–15.0 min) as compared to conventional adsorbents. This confirms the fast adsorption capacity of nanoparticles. Furthermore, the dose regimen of nanoparticles was also lower (in  $\mu\text{g/L}$ ) than conventional adsorbents. It is because of higher adsorption capacities of nanoparticles comparatively to conventional adsorbents. Besides, nanoparticles have been used for treating water under varied conditions of pHs (3–9). Generally, low cost adsorbents are effective for removing pollutants whose permissible limits are at milligram levels. Contrarily, nanoparticles can be used to remove water contaminants of microgram level permissible limits. For example, groundwater contamination due to arsenic is a worldwide problem. The WHO permissible limit of arsenic

is 10.0  $\mu\text{g/L}$ . This limit is seldom achieved in the groundwater by using low cost adsorbents. Contrarily, arsenic contamination has been reduced below the WHO permissible limit by using nanoparticle adsorbents. Similarly, other pollutants that can be removed by nanoparticles are cadmium, mercury, lead, selenium, pesticides, steroids, etc. due to their permitted ppb level limits. Briefly, in spite of some complications, my experience and observation compel me to consider nanoparticles as the need of the future in water treatment. These particles should be prepared in an eco-friendly way and used in a controlled way to avoid any environmental hazards. There is a great need to develop, optimize, and apply the new generated nanoparticles for water treatment at pilot and commercial levels by using column operations. Really, there is a demand of nanoparticles in water treatment due to poor water quality in many places of the world,<sup>55</sup> and the future of nanoparticles seems to be quite bright.

## 9. CONCLUSION

A critical evaluation of nanomaterials as adsorbents in this article indicates that nanoparticles have been used for the removal of metal ions, anions, and organic and biological species from water successfully. These particles are capable to remove pollutants even at low concentration, i.e.,  $\mu\text{g/L}$  under varied conditions of pH and temperature. The dose required of nanoparticles is quite low, making their application economical. Moreover, it has been observed that the removal time is quite fast, ranging from 1.0 to 15.0 min. These properties of nanoparticles made them ideal candidates for fast and inexpensive water treatment technology. It has also been observed that all the papers describe adsorption in batch process with quite good results, but no one deals at laboratory, pilot, and industrial scale columns, which are required urgently. Some workers coupled nanoparticles with other technologies for complete water treatment. This needs further research on nanoparticles for water treatment on a large scale. Some work has been carried out on this issue, and still there is a need for the development of novel nanomaterials with increased affinity, capacity, selectivity, and capability to work at column operations. The batch mode adsorption conditions should be transferred to column operations so that nano-adsorption technology may be utilized for the welfare of human beings. Besides, the management of the recovered pollutants and the exhausted nanoparticles has not been addressed in the literature. To avoid hazards of the recovered pollutants and nanotoxicology of used nanoparticles, the scientists should develop some eco-friendly waste management methods. To the best of my knowledge and experience, the future of nanoparticles in water treatment is quite bright, but it needs the collaborative efforts of research and industrial persons to materialize a dream of fast, economical, and feasible water treatment technology. By working together, it will be possible to solve water contamination globally.

## AUTHOR INFORMATION

### Corresponding Author

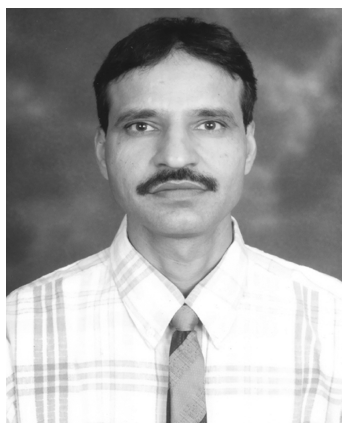
\*Phone: 091-9211458226. Fax: 0091-11-26985507 E-mail: drimran\_ali@yahoo.com, drimran.chiral@gmail.com. Web site: [http://old.jmi.ac.in/2000/Fnat/imran\\_ch.htm](http://old.jmi.ac.in/2000/Fnat/imran_ch.htm).

### Notes

The authors declare no competing financial interest.



## Biography



Dr. Imran Ali is an academican and researcher of international recognition at the Department of Chemistry, Jamia Millia Islamia (Central University), New Delhi, India. He obtained his M.Sc. and Ph.D. degrees in 1986 and 1990 from the Indian Institute of Technology, Roorkee, India. His research areas are bio-analytical chemistry, anticancer drugs development, and water treatment. He has published five books from Taylor & Francis, USA, John Wiley & Sons, USA, Marcel Dekker, Inc., USA, John Wiley & Sons, UK, and Elsevier, The Netherlands publishers. He has authored more than 250 publications. Dr. Ali's Scopus Citations is 2,700, and he is a leading worker in the area of chiral pollutants. A search on Google by chiral pollutants keyword indicates about all sites related to Dr. Imran Ali. He is Editor of ScienceJet Journal and on the editorial boards of 10 scientific journals. Dr. Ali is also a life member of five international scientific societies. He has enjoyed the positions of regular and visiting scientist in Saudi Arabia. He has also worked as a Visiting Professor in Oman. He is a widely travelled worker and has research collaborations in 12 countries. He is a reviewer of more than 50 international journals. His books and research papers are being used globally as standard reference sources.

## ACKNOWLEDGMENTS

Author is thankful to the administration of Jamia Millia Islamia (Central University), New Delhi, India, for providing infra-structures to write this article and carry out other research.

## ABBREVIATIONS

AFM	atomic force microscopy
CK	calcium and potassium
CNTs	carbon nanotubes
CTS/MMT	chitosan/montmorillonite
DETA	diethylenetriamine
DLVO	Derjaguin, Landau, Verwey, and Overbeek
DMA	dimethyl arsenic acid
DNA	deoxyribonucleic acid
DNPH	2,4-dinitrophenylhydrazine
ECH-RB5	epichlorohydrin-remazol black 5
ECH-3R	epichlorohydrin-3 red
FT-IR	Fourier transform infrared
GAC	granulated activated carbon
HA	humic acid
n-Hap	nanohydroxyapatite
HGMS	high gradient magnetic separation
IOCQ	iron oxide coated quartz
$\alpha$ -KA-CCMNP	$\alpha$ -ketoglutaric acid

NOM	natural organic matter
MIC	minimum inhibitory concentration
MMA	monomethyl arsenic acid
MWCNT	multiwalled carbon nanotubes
t-MWCNTs	thin multiwalled carbon nanotubes
NZVI	nanoscale zerovalent iron
PAP	poly(aspartate)
PSS	poly(styrene sulfonate)
ROS	reactive oxygen species
SEM	scanning electron microscopy
SWCNT	single-walled carbon nanotubes
TEM	transmission electron microscopy
TNT	titanate nanotubes
USSR	Union of Soviet Socialist Republics
WHO	World Health Organization
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

## REFERENCES

- (1) Nemerow, N.; Dasgupta, A. *Industrial and Hazardous Waste Treatment*, Van Nostrand Reinhold: New York, 1991.
- (2) Tchobanoglous, G.; Franklin, L. B. *Wastewater Engineering: Treatment, Disposal and Reuse*; McGraw Hill, Inc.: New York, 1991.
- (3) Ali, I.; Aboul-Enein, H. Y. *Chiral Pollutants: Distribution, Toxicity and Analysis by Chromatography and Capillary Electrophoresis*; John Wiley & Sons: Chichester, UK, 2004.
- (4) Franklin, L. B. *Wastewater Engineering: Treatment, Disposal and Reuse*, McGraw Hill Inc.: New York, 1991.
- (5) Droste, R. L. *Theory and Practice of Water and Wastewater Treatment*; John Wiley & Sons: New York, 1997.
- (6) John, D. Z. *Handbook of Drinking Water Quality: Standards and Controls*, Van Nostrand Reinhold: New York, 1990.
- (7) Laws, E. A. *Aquatic Pollution: An Introductory Text*, 3rd ed.; John Wiley & Sons: New York, 2000.
- (8) Ali, I.; Aboul-Enein, H. Y. *Instrumental Methods in Metal Ions Speciation: Chromatography, Capillary Electrophoresis and Electrochemistry*; Taylor & Francis Ltd.: New York, 2006.
- (9) Ali, I.; Aboul-Enein, H. Y.; Gupta, V. K. *Nano Chromatography and Capillary Electrophoresis: Pharmaceutical and Environmental Analyses*; John Wiley & Sons: Hoboken, NJ, 2009.
- (10) Vettorazzi, G. *International Regulatory Aspects for Pesticide Chemicals*; CRC Press Inc.: Boca Raton, FL, 1979; Vol. 1, p14.
- (11) Duffus, J. H. *Pure Appl. Chem.* **2002**, 74, 793.
- (12) Jain, C. K.; Ali, I. *Water Res.* **2000**, 34, 4304.
- (13) Yamamura, Y.; Yamauchi, H. *Ind. Health* **1980**, 18, 203.
- (14) Kipping, M. D. In *Arsenic, the Chemical Environment, Environment and Man*; Lenihan, J., Fletcher, W. W., Eds.; World Health Organization: Glasgow, UK, 1977; Vol. 6.
- (15) *Environmental Health Criteria*, 18: *Arsenic*; World Health Organization: Geneva, 1981.
- (16) Pershagen, G. *The Epidemiology of Human Arsenic Exposure*; Fowler, B. A., Ed.; Elsevier: Amsterdam, The Netherlands, 1983.
- (17) Csanady, M.; Straub, I. Health Damage Due to Pollution in Hungary. Proceedings of the Rome Symposium, September, 1994; International Association of Hydrological Sciences: Wallingford, Oxfordshire, UK, 1995; Publ. No. 233.
- (18) Matschullat, J. *Sci. Total Environ.* **2000**, 249, 297.
- (19) Ng, J. C.; Wang, J.; Shrain, A. *Chemosphere* **2003**, 52, 1353.
- (20) Zhu, C.; Luan, Z.; Wang, Y.; Shan, X. *Sep. Purif. Technol.* **2007**, 57, 161.
- (21) Marin, A. B. P.; Zapata, V. M.; Orturao, J. F.; Aguilar, M.; Saez, J.; Lloren, M. J. *Hazard. Mater.* **2007**, 139, 122.
- (22) Zhang, F. S.; Nriagu, J. O.; Itoh, H. *Water. Res.* **2005**, 39, 389.
- (23) Ruiz, C. G. *Bioresour. Technol.* **2006**, 97, 1907.
- (24) Bayramoglu, G.; Arica, M. Y. *J. Hazard. Mater.* **2007**, 144, 449.
- (25) Sigel, H.; Sigel, A. *Concepts on Metal Ion Toxicity*; Marcel Dekker, Inc.: New York, 1986.

- (26) Suhasini, I. P.; Sriram, G.; Asolekar, S. R.; Sureshkumar, G. K. *Process Biochem.* **1999**, *34*, 239.
- (27) Rengaraj, S.; Moon, S. H. *Water Res.* **2002**, *36*, 1783.
- (28) Smiciklas, I.; Dimovic, S.; Plecas, I.; Mitrio, M. *Water Res.* **2006**, *40*, 2267.
- (29) Vatisstas, N.; Bartolozzi, M. J. *Power Sources* **1999**, *79*, 199.
- (30) Weng, C. H.; Huang, C. P. *Colloids Surf., A* **2004**, *247*, 137.
- (31) Oren, A. H.; Kaya, A. J. *Hazard. Mater.* **2006**, *131*, 59.
- (32) Kross, B. C.; Ayebo, A. D.; Fuortes, L. J. *Am. Fam. Physician* **1992**, *46*, 183.
- (33) *Guidelines for Drinking-Water Quality*, 2nd ed.; World Health Organization: Geneva, 1993; Vol. 1.
- (34) Meyers, R. A., Ed. *Encyclopedia of Environmental Pollution and Clean-up*; John Wiley & Sons: New York, 1999.
- (35) Damia, B., Ed. *Emerging Organic Pollutants in Waste Waters and Sludge*; Springer: New York, 2005.
- (36) *Persistent Organic Pollutants: Impact on Child Health*; NLM classification: WA 671, WHO report; World Health Organization: Geneva, 2010.
- (37) Köhler, A.; Hellweg, S.; Escher, B. I.; Hungerbühler, K. *Environ. Sci. Technol.* **2006**, *40*, 3395.
- (38) Gadd, G. M.; Griffiths, A. J. *Microb. Ecol.* **1978**, *4*, 303.
- (39) Gledhill, W. E. *Toxicol. Assess.* **1987**, *2*, 89.
- (40) Dyson, T. *Population and Food: Global Trends and Future Prospects*; Routledge: London, 1996.
- (41) Weber, B.; Holz, F. *Landfill Leachates Treatment by Reverse Osmosis, In Effective Industrial Membrane Processes, Benefits and Opportunities*; Turner, M. K., Ed.; Elsevier Science Publishers Ltd.: Barking, Essex, UK, 1991.
- (42) Williams, A. R. *The Use of Reverse Osmosis for the Purification of Coal Gasification Liquors, In Effective Industrial Membrane Processes, Benefits and Opportunities*; Turner, M. K., Ed.; Elsevier science Publishers Ltd.: Barking, Essex, UK, 1991.
- (43) Zinkus, G. A.; Byers, W. D.; Doerr, W. W. *Chem. Eng. Prog.* **1998**, *94*, 19.
- (44) Ali, I.; Khan, T. A.; Asim, M. *Sep. Purif. Rev.* **2011**, *40*, 25.
- (45) Koros, W. J. *Chem. Eng. Prog.* **1995**, *91*, 68.
- (46) Coin, R. J.; Niksa, M. J.; Elyanow, D. I. *Environ. Prog.* **1996**, *15*, 122.
- (47) Lin, S. H.; Chen, M. L. *Water Res.* **1997**, *31*, 868.
- (48) Zor, S.; Yazici, B.; Erbil, M.; Galip, H. *Water Res.* **1998**, *32*, 579.
- (49) Saleh, T. A.; Gupta, V. K. *Environ. Sci. Pollut. Res.* **2012**, *19*, 1224.
- (50) Gupta, V. K.; Nayak, A. *Chem. Eng. J.* **2012**, *180*, 81.
- (51) Gupta, V. K.; Saleh, T. A. J. *Colloids Interface Sci.* **2011**, *362*, 344.
- (52) Saleh, T. A.; Agarwal, S.; Gupta, V. K. *Appl. Catal., B* **2011**, *106*, 46.
- (53) Gupta, V. K.; Saleh, T. A. *Water Res.* **2011**, *45*, 2207.
- (54) Gupta, V. K.; Agarwal, S.; Saleh, T. A. J. *Hazard. Mater.* **2011**, *185*, 17.
- (55) Ali, I.; Gupta, V. K. *Adsorbents for Water Treatment: Development of Low-Cost Alternatives to Carbon. Encyclopedia of Surface and Colloid Science*, 2nd ed.; Taylor & Francis: New York, 2006; pp 149–184.
- (56) Ali, I.; Jain, C. K. *Wastewater treatment and recycling technologies. In Water Encyclopedia: Domestic, Municipal, And Industrial Water Supply and Waste Disposal*; Lehr, J., Ed.; John Wiley & Sons: New York, 2005.
- (57) Faust, S. D.; Aly, O. M. *Chemistry of Water Treatment*, Butterworth: Stoneham, MA, 1983.
- (58) Masel, R. I. *Principles of Adsorption and Reaction on Solid Surfaces*; John Wiley & Sons: New York, 1996.
- (59) Condon, J. B. *Surface Area and Porosity Determinations by Physorption: Measurements and Theory*; Elsevier: New York, 2006.
- (60) Barbosa-Cánovas, G. V.; Vega-Mercado, H. *Dehydration of Foods*; Chapman & Hall: New York, 1996.
- (61) Lewinsky, A. A. *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*, Nova Science Publishers: New York, 2007.
- (62) Brinker, C. J.; Scherer, W. J. *Sol-Gel Science*; Academic Press: New York, 1990.
- (63) Palkar, V. R. *Nanostruct. Mater.* **1999**, *11*, 369.
- (64) Bessekhouad, Y.; Robert, D.; Weber, J. V. *Int. J. Photoenergy* **2003**, *5*, 153.
- (65) Kornak, R.; Niznansky, D.; Haimann, K.; Tylus, W.; Maruszewski, K. *Mater. Sci.* **2005**, *23*, 87.
- (66) Sarkar, D.; Mohapatra, D.; Roy, S.; Bhattacharya, S.; Adak, S.; Mitra, N. *Ceram. Int.* **2007**, *33*, 1275.
- (67) Azadmanjiri, J. J. *Non-Cryst. Solids* **2007**, *353*, 4170.
- (68) Ramsden, J. *Nanotechnology: An Introduction*, Elsevier: The Netherlands, 2011.
- (69) Binns, C. *Introduction to Nanoscience and Nanotechnology*; Wiley & Sons: New York, 2010.
- (70) Chi, L., Ed. *Nanotechnology: Volume 8, Nanostructured Surfaces*; John Wiley & Sons: New York, 2010.
- (71) Fahrner, W. *Nanotechnology and Nanoelectronics Materials, Devices, Measurement Techniques*; Springer: New York, 2005.
- (72) Kiss, L. B.; Söderlund, J.; Niklasson, G. A.; Granqvist, C. G. *Nanotechnology* **1999**, *10*, 25.
- (73) Buzea, C.; Pacheco, I.; Robbie, K. *Biointerphases* **2007**, *2*, MR17.
- (74) Deliyanni, E. A.; Lazaridis, N. K.; Peleka, E. N.; Matis, K. A. *Environ. Sci. Pollut. Res.* **2004**, *11*, 18.
- (75) Huang, Y. H.; Hsueh, C. I.; Cheng, H. P.; Su, L. C.; Chen, C. Y. *J. Hazard. Mater.* **2006**, *144*, 406.
- (76) Johnson, B. B. *Environ. Sci. Technol.* **1990**, *24*, 112.
- (77) Charlet, M. L. J. *Colloid Interface Sci.* **1994**, *168*, 87.
- (78) Venema, P.; Hiemstra, T.; Weidlu, P. G.; Riemsdijk, W. H. V. J. *Colloid Interface Sci.* **1998**, *198*, 282.
- (79) Zeng, L. *Water Res.* **2003**, *37*, 4351.
- (80) Pokhrel, D.; Viraraghavan, T. *Bioresour. Technol.* **2007**, *99*, 2067.
- (81) Fendrof, S.; Eick, M. J.; Grossl, P.; Sparks, D. L. *Environ. Sci. Technol.* **1997**, *31*, 315.
- (82) Dixit, S.; Hering, J. G. *Environ. Sci. Technol.* **2003**, *37*, 4182.
- (83) Ponder, S. M.; Darab, J. G. *Environ. Sci. Technol.* **2000**, *34*, 2564.
- (84) Kanel, S. R.; Charlet, B.; Choi, L. *Environ. Sci. Technol.* **2005**, *39*, 1291.
- (85) Ponder, S. M.; Darab, J. G.; Bucher, J. D.; Craig, C. I.; Davis, L.; Stein, N. E.; Lukens, W.; Nitsche, H.; Rao, L. F.; Shuh, D. K.; Mallouk, T. E. *Sep. Purif. Technol.* **2007**, *57*, 161.
- (86) Ayuso, E. A.; Sanchez, A. G.; Querol, X. J. *Hazard. Mater.* **2007**, *142*, 191.
- (87) Valente, S.; Bokhimi, X.; Toledo, J. A. *Appl. Catal., A* **2004**, *264*, 175.
- (88) Baumgarten, E.; Dusing, U. K. J. *Colloid Interface Sci.* **1994**, *194*, 1.
- (89) Pacheco, S.; Rodriguez, R. J. *Sol–Gel Sci. Technol.* **2001**, *20*, 263.
- (90) Brammer, H.; Ravenscroft, P. *Environ. Int.* **2009**, *35*, 647.
- (91) Khan, A. W.; Ahmad, A.; Sayed, S. U.; Hadi, A.; Khan, M. H.; Jalil, M. A.; Ahmed, R.; Faruquee, M. H. J. *Soc. Prev. Med.* **1997**, *16*, 65.
- (92) Dhar, R. K.; Biswas, B. K.; Samanta, G.; Mandal, B. K.; Chowdhury, R. T.; Chanda, C. R.; Basu, G.; Chakraborti, D.; Roy, S.; Kabir, S. *Groundwater arsenic contamination and sufferings of people in Bangladesh may be the biggest arsenic calamity in the world. Paper presented at the ; International Conference on Arsenic Pollution of Groundwater in Bangladesh: Causes, Effects and Remedies*, Dhaka, Bangladesh, February 8–12, 1998.
- (93) Chatterjee, A.; Das, D.; Mandal, B. K.; Chowdhury, T. R.; Samanta, G.; Chakraborti, D. *Analyst* **1995**, *120*, 643.
- (94) Das, D.; Chatterjee, A.; Mandal, B. K.; Samanta, C.; Chakraborti, D.; Chanda, B. *Analyst* **1995**, *120*, 917.
- (95) Deliyanni, E. A.; Bakoyannakis, D. N.; Zouboulis, A. I.; Matis, K. A. *Chemosphere* **2003**, *50*, 155.
- (96) Deliyanni, E. A.; Nalbandian, L. K.; Matis, A. J. *Colloid Interface Sci.* **2006**, *302*, 458.
- (97) Pena, M. E.; Koratis, G. P.; Patel, M.; Lippincott, L.; Meng, X. *Water Res.* **2005**, *39*, 2327.
- (98) Kanel, S. R.; Greneche, J. M.; Choi, H. *Environ. Sci. Technol.* **2006**, *40*, 2040.
- (99) Hristovski, K.; Baumgardener, A.; Westerhoff, P. J. *Hazard. Mater.* **2007**, *147*, 265.

- (100) Zhu, H. J.; Jia, Y. F.; Wu, X.; Wang, H. *Huan Jing Ke Xue* **2009**, *30*, 1644.
- (101) Zhu, H. J.; Jia, Y. F.; Yao, S. H.; Wu, X.; Wang, S. Y. *Huan Jing Ke Xue* **2009**, *30*, 3562.
- (102) Zhu, H.; Jia, Y.; Wu, X.; Wang, H. *J. Hazard. Mater.* **2009**, *172*, 1591.
- (103) Mostafa, M. G.; Chen, Y. H.; Jean, J. S.; Liu, C. C.; Teng, H. *Water Sci. Technol.* **2010**, *62*, 378.
- (104) Chowdhury, S. R.; Yanful, E. K. *J. Environ. Manage.* **2010**, *91*, 2238.
- (105) Jegadeesan, G.; Al-Abed, S. R.; Sundaram, V.; Choi, H.; Scheckel, K. G.; Dionysiou, D. D. *Water Res.* **2010**, *44*, 965.
- (106) Skubul, L. R.; Meshkov, N. K.; Rajh, T.; Thurnaur, M. J. *Photochem. Photobiol., A* **2002**, *148*, 393.
- (107) Lazaridis, N. K.; Bakoyannakis, D. N.; Deliyanni, E. A. *Chemosphere* **2005**, *58*, 65.
- (108) Gao, Y.; Wahi, R.; Kan, A. T.; Falkner, J. C.; Colvin, V. L.; Tomson, M. B. *Langmuir* **2004**, *20*, 9585.
- (109) Deliyanni, E. A.; Matis, K. A. *Sep. Purif. Technol.* **2005**, *45*, 96.
- (110) Pacheco, S.; Tapia, J.; Medina, M.; Rodriguez, R. J. *Non-Cryst. Solids* **2006**, *352*, 5475.
- (111) Shao-Feng, N.; Yong, L.; Xin-hua, X.; Zhang-hua, L. *J. Zhejiang Univ. Sci. B* **2005**, *6*, 1022.
- (112) Hu, J.; Chen, G.; Lo, I. M. C. *Water Res.* **2005**, *39*, 4528.
- (113) Hu, J.; Chen, G.; Lo, I. M. C. *J. Environ. Eng.* **2006**, *132*, 709.
- (114) Hu, J.; Lo, I. M. C.; Chen, G. *Sep. Purif. Technol.* **2007**, *56*, 249.
- (115) Guan, X. H.; Qin, Y. C.; Qin, Y. H.; Yin, R.; Sun, M. J. *Huan Jing Ke Xue* **2007**, *28*, 2096.
- (116) Chang, Y. C.; Chang, S. W.; Chen, D. H. *React. Funct. Polym.* **2006**, *66*, 335.
- (117) Uheida, A.; Alvarz, G. S.; Bijorkman, E.; Yu, Z.; Muhammed, M. J. *Colloid Interface Sci.* **2006**, *298*, 501.
- (118) Ajmal, M.; Khan, A. H.; Ahmad, S.; Ahmad, A. *Water Res.* **1998**, *32*, 3085.
- (119) Deng, S.; Bai, R.; Chen, J. P. *Langmuir* **2003**, *19*, 5058.
- (120) Sun, C.; Qu, R.; Ji, C.; Wang, C.; Sun, Y.; Yue, Z.; Cheng, G. *Talanta* **2006**, *70*, 14.
- (121) Chang, Y. C.; Chen, D. H. *J. Colloid Interface Sci.* **2005**, *283*, 446.
- (122) Banerjee, S. S.; Chen, D. H. *J. Hazard. Mater.* **2007**, *147*, 792.
- (123) Gandhi, M. R.; Kousalya, G. N.; Meenakshi, S. *Int. J. Biol. Macromol.* **2010**, *48*, 119.
- (124) Hao, Y. M.; Man, C.; Hu, Z. B. *J. Hazard. Mater.* **2010**, *184*, 392.
- (125) Chen, Y. H.; Li, F. A. *J. Colloid Interface Sci.* **2010**, *347*, 277.
- (126) Zhang, L.; Liu, N.; Yang, L.; Lin, Q. *J. Hazard. Mater.* **2009**, *170*, 1197.
- (127) Pan, B.; Xiao, L.; Nie, G.; Pan, B.; Wu, J.; Lv, L.; Zhang, W.; Zheng, S. *J. Environ. Monit.* **2010**, *12*, 305.
- (128) Zhang, Q.; Pan, B.; Pan, B.; Zhang, W.; Jia, K.; Zhang, Q. *Environ. Sci. Technol.* **2008**, *42*, 4140.
- (129) Afkhami, A.; Saber-Tehrani, M.; Bagheri, H. *J. Hazard. Mater.* **2010**, *181*, 836.
- (130) Deliyanni, E. A.; Peleka, E. N.; Matis, K. A. *J. Hazard. Mater.* **2007**, *141*, 176.
- (131) Sairam, S. C.; Viswanathan, N.; Meenakshi, S. *J. Hazard. Mater.* **2008**, *155*, 206.
- (132) Sairam, S. C.; Viswanathan, N.; Meenakshi, S. *J. Hazard. Mater.* **2009**, *172*, 147.
- (133) Bhatnagar, A.; Kumar, E.; Sillanpää, M. *Chem. Eng. J.* **2010**, *163*, 317.
- (134) Kassaei, M. Z.; Motamedi, E.; Mikhak, A.; Rahnemaie, R. *Chem. Eng. J.* **2011**, *166*, 490.
- (135) Martin, B. D.; Parsons, S. A.; Jefferson, B. *Water Sci. Technol.* **2009**, *60*, 2637.
- (136) Xi, H. B.; Yang, Q.; Shang, H. T.; Hao, C. B.; Li, Z. L. *Huan Jing Ke Xue* **2008**, *29*, 2529.
- (137) Huang, S. H.; Chen, D. H. *J. Hazard. Mater.* **2009**, *163*, 174.
- (138) Belessi, V.; Romanos, G.; Boukos, N.; Lambropoulou, D.; Trapalis, C. *J. Hazard. Mater.* **2009**, *170*, 836.
- (139) Moussavi, G.; Mahmoudi, M. *J. Hazard. Mater.* **2009**, *168*, 806.
- (140) Chen, C. Y.; Chang, J. C.; Chen, A. H. *J. Hazard. Mater.* **2011**, *185*, 430.
- (141) Chang, Y. C.; Chen, D. H. *Macromol. Biosci.* **2005**, *254*, 61.
- (142) Cheung, W. H.; Szeto, Y. S.; McKay, G. *Bioresour. Technol.* **2007**, *98*, 2897.
- (143) Wang, L.; Wang, A. *J. Hazard. Mater.* **2007**, *147*, 979.
- (144) Du, W. L.; Xu, Z. R.; Han, X. Y.; Xu, Y. L.; Miao, Z. G. *J. Hazard. Mater.* **2008**, *153*, 152.
- (145) Zhao, M.; Tang, Z.; Liu, P. *J. Hazard. Mater.* **2008**, *158*, 43.
- (146) Sandoval, R.; Cooper, A. M.; Aymar, K.; Jain, A.; Hristovski, K. *J. Hazard. Mater.* **2011**, *193*, 296.
- (147) Iram, M.; Guo, C.; Guan, Y.; Ishfaq, A.; Liu, H. *J. Hazard. Mater.* **2010**, *181*, 1039.
- (148) Ali, I.; Jain, C. K. *Curr. Sci.* **1998**, *75*, 1011.
- (149) Li, Y.; Lu, J. J.; Shi, B. Y.; Wu, Y. Y. *Huan Jing Ke Xue* **2008**, *29*, 1687.
- (150) Yang, K.; Xing, B. *Environ. Sci. Technol.* **2009**, *43*, 1845.
- (151) Yang, K.; Zhu, L.; Xing, B. *Environ. Sci. Pollut. Res. Int.* **2010**, *17*, 410.
- (152) Shen, L. L.; Zhao, B. Z.; Zhang, J. B.; Chen, J.; Zheng, H. *Huan Jing Ke Xue* **2010**, *31*, 983.
- (153) Li, Z.; Greden, K.; Alvarez, P. J.; Gregory, K. B.; Lowry, G. V. *Environ. Sci. Technol.* **2010**, *44*, 3462.
- (154) Li, Y. H.; Wang, S.; Luan, Z.; Ding, J.; Xu, C.; Wu, D. *Carbon* **2003**, *41*, 1057.
- (155) Singh, D. B.; Rupainwar, D. C.; Prasad, G.; Jayaprakas, K. C. *J. Hazard. Mater.* **1998**, *60*, 29.
- (156) Li, Y. H.; Di, Z.; Ding, J.; Wu, D.; Luan, Z.; Zhu, Y. *Water Res.* **2005**, *39*, 605.
- (157) Kochkar, H.; Turki, A.; Bergaoui, L.; Berhault, G.; Ghorbel, A. *J. Colloid Interface Sci.* **2009**, *331*, 27.
- (158) Yang, S. H.; Shin, W. H.; Kang, J. K. *J. Chem. Phys.* **2006**, *125*, 084705.
- (159) Lu, C.; Chiu, H. *Chem. Eng. Sci.* **2006**, *61*, 1138.
- (160) Di, Z. C.; Ding, J.; Peng, X. J.; Li, Y. H.; Laun, Z. K.; Liang, J. *Chemosphere* **2006**, *62*, 861.
- (161) Doong, R. A.; Chiang, L. F. *Water Sci. Technol.* **2008**, *58*, 1985.
- (162) Stafiej, A.; Pyrzyńska, K. *Sep. Purif. Technol.* **2007**, *58*, 49.
- (163) Wang, H.; Zhou, A.; Peng, F.; Yu, H.; Yang, J. *J. Colloid Interface Sci.* **2007**, *316*, 277.
- (164) Wu, C. H. *J. Colloid Interface Sci.* **2007**, *311*, 338.
- (165) Lou, J. C.; Jung, M. J.; Yang, H. W.; Han, J. Y.; Huang, W. H. *J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng.* **2011**, *46*, 1357.
- (166) Machado, F. M.; Bergmann, C. P.; Fernandes, T. H.; Lima, E. C.; Royer, B.; Calvete, T.; Fagan, S. B. *J. Hazard. Mater.* **2011**, *192*, 1122.
- (167) Shim, W. G.; Balathanigaimani, M. S.; Lee, S. G.; Kim, S. C.; Moon, H. *J. Nanosci. Nanotechnol.* **2010**, *10*, 3680.
- (168) Moeser, G. D.; Roach, K. A.; Green, W. H.; Hatton, T. A. *AIChE J.* **2004**, *50*, 2835.
- (169) Kim, S.; Marion, M.; Jeong, B. H.; Hoek, E. M. V. *J. Membr. Sci.* **2006**, *284*, 361.
- (170) McDonogh, R. M.; Fell, C. J. D.; Fane, A. G. *J. Membr. Sci.* **1984**, *21*, 285.
- (171) Chen, G.; Wang, Y.; Tan, L. H. M.; Yang, X.; Tan, L. S.; Chen, Y.; Chen, H. Y. *J. Am. Chem. Soc.* **2009**, *131*, 4218.
- (172) Sun, X. M.; Tabakman, S. M.; Seo, W. S.; Zhang, L.; Zhang, G. Y.; Sherlock, S.; Bai, L.; Dai, H. *J. Angew. Chem., Int. Ed.* **2009**, *48*, 939.
- (173) Bai, L.; Ma, X. J.; Liu, J. F.; Sun, X. M.; Zhao, D. Y.; Evans, D. G. *J. Am. Chem. Soc.* **2010**, *132*, 233.
- (174) Wu, T.; Wang, X. J.; Li, G. P.; Chen, T.; Yang, M. X.; Zhang, Z.; Chen, H. Y. *Nano Lett.* **2008**, *8*, 2643.
- (175) Chen, H. Y.; Wang, Y.; Chen, G.; Yang, M. X.; Silber, G.; Xing, S. X.; Tan, L. H.; Wang, F.; Feng, Y. H.; Liu, X. G.; Li, S. Z. *Nature Commun.* **2010**, *1*, 1.



- (176) Qiu, P.; Mao, C. *Adv. Mater.* **2011**, *23*, 4880.
- (177) Uheida, A.; Iglesias, M.; Fontàs, C.; Hidalgo, M.; Salvadó, V.; Zhang, Y.; Muhammed, M. J. *Colloid Interface Sci.* **2006**, *301*, 402.
- (178) Hu, J.; Lo, I. M. C.; Chen, G. *Sep. Purif. Technol.* **2007**, *58*, 76.
- (179) Namdeo, M.; Bajpai, S. K. *Electron. J. Environ. Agric. Food Chem.* **2008**, *7*, 3082.
- (180) Hu, J.; Lo, I. M. C.; Chen, G. H. *Langmuir* **2005**, *21*, 11173.
- (181) Ryman-Rasmussen, J. P.; Riviere, J. E.; Monteiro-Riviere, N. A. *Toxicol. Sci.* **2006**, *91*, 159.
- (182) Oberdörster, G.; Maynard, A.; Donaldson, K.; Castranova, V.; Fitzpatrick, J.; Ausman, K.; Carter, J.; Karn, B.; Kreyling, W.; Olin, L. S.; Monteiro-Riviere, N.; Warheit, W.; Yang, H. *Part. Fibre Toxicol.* **2005**, *2*, 8.
- (183) Peter, H. M.; Bröske-Hohlfeld, I.; V Salata, O. J. *Nanobiotechnology* **2004**, *2*, 12.
- (184) Oberdörster, G.; Oberdörster, E.; Oberdorster, J. *Environ. Health Perspect.* **2005**, *113*, 823.
- (185) Li, N.; Sioutas, C.; Cho, A.; Schmitz, D.; Misra, C.; Sempf, J.; Wang, M.; Oberley, T.; Froines, J.; Nel, A. *Environ. Health Perspect.* **2003**, *111*, 455.
- (186) Porter, A. E.; Gass, M.; Muller, K.; Skepper, J. N.; Midgley, P.; Welland, M. *Environ. Sci. Technol.* **2007**, *41*, 3012.
- (187) Geiser, M.; Rothen-Rutishauser, B.; Kapp, N.; Schürch, S.; Kreyling, W.; Schulz, H.; Semmler, M.; Hof, V. I.; Heyder, J.; Gehr, P. *Environ. Health Perspect.* **2005**, *113*, 1555.
- (188) Nel, A.; Xia, T.; Madler, L.; Li, N. *Science* **2006**, *311*, 622.
- (189) Savić, R.; Luo, L.; Eisenberg, A.; Maysinger, D. *Science* **2003**, *300*, 615.
- (190) Zook, J. M.; Maccuspie, R. I.; Locascio, L. E.; Halter, M. D.; Elliott, J. T. *Nanotoxicology* **2011**, *5*, 517.
- (191) Hristozov, D. R.; Gottardo, S.; Critto, A.; Marcomini, A. *Nanotoxicology* **2012**, DOI: 10.3109/17435390.2011.626534.
- (192) Arora, S.; Rajwade, J. M.; Paknikar, K. M. *Toxicol. Appl. Pharmacol.* **2012**, *258*, 151.
- (193) Petersen, E. J.; Henry, T. B. *Environ. Toxicol. Chem.* **2012**, *31*, 60.
- (194) Ai, J.; Biazar, E.; Jafarpour, M.; Montazeri, M.; Majdi, A.; Aminifard, S.; Zafari, M.; Akbari, H. R.; Rad, H. G. *Int. J. Nanomed.* **2011**, *6*, 1117.
- (195) Castranova, V. J. *Occup. Environ. Med.* **2011**, *53*, S14.
- (196) Grieger, K. D.; Linkov, I.; Hansen, S. F.; Baun, A. *Nanotoxicology* **2012**, *6*, 196.
- (197) Hubbs, A. F.; Mercer, R. R.; Benkovic, S. A.; Harkema, J.; Sriram, K.; Schwegler-Berry, D.; Goravanahally, M. P.; Nurkiewicz, T. R.; Castranova, V.; Sargent, L. M. *Toxicol. Pathol.* **2011**, *39*, 301.
- (198) Clark, K. A.; White, R. H.; Silbergeld, E. K. *Regul. Toxicol. Pharmacol.* **2011**, *59*, 361.
- (199) Buzea, C.; Pacheco, I. I.; Robbie, K. *Biointerphases* **2007**, *2*, MR17.
- (200) Fauré, J.; Lachenal, G.; Court, M.; Hirrlinger, J.; Chatellard-Causse, C.; Blot, B.; Grange, J.; Schoehn, G.; Goldberg, Y.; Boyer, V.; Kirchhoff, F.; Raposo, G.; Garin, J.; Sadoul, R. *Mol. Cell. Neurosci.* **2006**, *31*, 642.
- (201) Schmidt-Ott, A.; Butselaar-Orthlieb, V.; van Winsen, J.; Bosma, D. *Nanosafety Guidelines: Preventing Exposure to Nanomaterials at the Faculty of Applied Sciences, Delft University of Technology, Workgroup Nanosafety of the Faculty of Applied Sciences; Delft University of Technology: Delft, The Netherlands*, 2010.
- (202) Bennett, D.; Chi, S. *Stakeholder's Attitudes Towards the European Code of Conduct for Nanosciences & Nanotechnologies Research, Delft University of Technology, The Netherlands; Delft University of Technology: Delft, The Netherlands*, www.nanocode.eu.
- (203) ASTM International standards; ASTM International: West Conshohocken, PA; <http://www.astm.org/>.
- (204) Gatti, A. M. *Nanotoxicity and Health Risk Related to Managing Nanoparticles the European Experience of Nanopathology*; University of Modena and Reggio Emilia, Laboratory of Biomaterials: Modena, Italy, 2005.
- (205) Hoet, P. H. M.; Bröske-Hohlfeld, I.; Salata, O. V. J. *Nanobiotechnol.* **2004**, *2*, 12.
- (206) Mnyusiwalla, A.; Daar, A. S.; Singer, P. A. *Nanotechnology* **2003**, *14*, 9.
- (207) Ali, I. *Sep. Purif. Rev.* **2010**, *39*, 95.
- (208) Zeng, W. M.; Gao, L.; Guo, J. K. *Nanostruct. Mater.* **1998**, *10*, 543.
- (209) Park, Y. K.; Tadd, E. H.; Zubris, M.; Tannenbaum, R. *Mater. Res. Bull.* **2005**, *40*, 1506.
- (210) Jin, W.; Lee, I. K.; Kompch, A.; Dörfler, U.; Winterer, M. *J. Eur. Ceram. Soc.* **2007**, *27*, 4333.
- (211) Biasi, R. S. D.; Figueiredo, A. B. S.; Fernandes, A. A. R.; Larica, C. *Solid State Commun.* **2007**, *144*, 15.
- (212) Oh, H.; Kim, S. J. *Aerosol. Sci.* **2007**, *44*, 1185.
- (213) Han, D.; Yang, H.; Zhu, C.; Wang, F. *Powder Technol.* **2008**, *185*, 286.
- (214) Hullavarad, N. V.; Hullavarad, S. S. *Photonics Nanostruct.: Fundam. Appl.* **2007**, *5*, 156.
- (215) Okitsu, K.; Mizukoshi, Y.; Yamamoto, T. A.; Maeda, Y.; Nagata, Y. *Mater. Lett.* **2007**, *61*, 3429.
- (216) Dong, S.; Zhou, S. *Mater. Sci. Eng., B* **2007**, *140*, 153.
- (217) Dong, S.; Yang, S.; Tang, C. *Chem. Res. Chin. Univ.* **2007**, *23*, 500.
- (218) Ban, I.; Drofenik, M.; Makovec, D. J. *Magn. Magn. Mater.* **2006**, *307*, 250.
- (219) Takami, S.; Sato, T.; Mousavand, T.; Ohara, S. I.; Umetsu, M.; Adschiri, T. *Mater. Lett.* **2007**, *61*, 4769.
- (220) Zawrah, M. F. M.; Kheshen, A. A. E. *Br. Ceram. Trans.* **2002**, *101*, 71.
- (221) Thota, S.; Kumar, J. J. *Phys. Chem. Solids* **2007**, *68*, 1951.
- (222) Chrusciel, J.; Slusarski, L. *Mater. Sci.* **2003**, *21*, 461.
- (223) Ibarguen, C.; Mosquera, A. A.; Parra, R.; Castro, M. S.; Rodríguez-Páez, J. E. *Mater. Chem. Phys.* **2007**, *101*, 433.
- (224) Kitamura, Y.; Okinaka, N.; Shibayama, T.; Mahaney, O. O. P.; Kusano, D.; Ohtani, B.; Akiyama, T. *Powder Technol.* **2007**, *176*, 93.
- (225) Figgemeier, E.; Kylberg, W.; Constable, E.; Scarisoreanu, M.; Alexandrescu, R.; Morjan, I.; Soare, I.; Birjega, R.; Popovici, E.; Fleaca, C.; Gavrilă-Florescu, L.; Prodan, G. *Appl. Surf. Sci.* **2007**, *254*, 1037.
- (226) Kim, C. S.; Kwon, I. M.; Moon, B. K.; Jeong, J. H.; Choi, B. C.; Kim, J. H.; Choi, H.; Yi, S.; Yoo, D. H.; Hong, K. S.; Park, J. H.; Lee, H. S. *Mater. Sci. Eng., C* **2007**, *27*, 1343.
- (227) Zhai, Y.; Gao, Y.; Liu, F.; Zhang, Q.; Gao, G. *Mater. Lett.* **2007**, *61*, 5056.
- (228) Kandjani, A. E.; Tabriz, M. F.; Pourabbas, B. *Mater. Res. Bull.* **2008**, *43*, 645.
- (229) Bhattacharjee, B.; Ganguli, D.; Chaudhuri, S.; Pal, A. K. *Mater. Chem. Phys.* **2003**, *78*, 372.
- (230) Thareja, R. K.; Shukla, S. *Appl. Surf. Sci.* **2007**, *253*, 8889.
- (231) Patil, P. R.; Joshi, S. S. *Mater. Chem. Phys.* **2007**, *105*, 354.
- (232) Guo, G. Y.; Chen, Y. L. *J. Solid State Chem.* **2005**, *178*, 1675.
- (233) Weng, C. H.; Wang, J. H.; Huang, C. P. *Water Sci. Technol.* **1997**, *35*, 55.
- (234) Zheng, Y. M.; Yu, L.; Wu, D.; Chen, J. P. *Chem. Eng. J.* **2012**, *188*, 15.
- (235) Mayo, J. T.; Yavuz, C.; Yean, S.; Cong, L.; Shipley, H.; Yu, W.; Falkner, J.; Kan, A.; Tomson, M.; Colvin, V. L. *Sci. Technol. Adv. Mater.* **2007**, *8*, 71.
- (236) Dousova, B.; Grygar, T.; Martaus, A.; Fuitova, L.; Kolousek, D.; Machovi, V. J. *Colloid Interface Sci.* **2006**, *302*, 424.
- (237) Chang, Y. C.; Chen, D. H. J. *Colloid Interface Sci.* **2005**, *283*, 446.
- (238) Shin, K. Y.; Hong, J. Y.; Jang, J. J. *Hazard. Mater.* **2011**, *190*, 36.
- (239) Pacheco, S.; Medina, M.; Valencia, F.; Tapia, J. J. *Environ. Eng.* **2006**, *132*, 342.
- (240) Song, J.; Kong, H.; Jang, J. J. *Colloid Interface Sci.* **2011**, *359*, 505.
- (241) Fan, L.; Luo, C.; Zhen, L. V.; Lu, F.; Qiu, H. *Colloids Surf. B* **2011**, *88*, 574.

- (242) Shengdong, P.; Haoyu, S.; Qihong, X.; Jian, L.; Meiqin, H. *J. Colloid Interface Sci.* **2012**, *365*, 204.
- (243) Chiou, M. S.; Chuang, G. S. *Chemosphere* **2006**, *62*, 731.
- (244) Stephen Inbaraj, B.; Chen, B. H. *Bioresour. Technol.* **2011**, *102*, 8868.
- (245) Wu, D.; Zheng, P.; Chang, P. R.; Ma, X. *Chem. Eng. J.* **2011**, *174*, 489.
- (246) Zhang, Z.; Kong, J. J. *Hazard. Mater.* **2011**, *193*, 325.
- (247) Giri, S. K.; Das, N. N.; Pradha, G. C. *Colloids Surf. A* **2011**, *389*, 43.
- (248) Chen, Y. H. *J. Non-Cryst. Solids* **2011**, *357*, 136.
- (249) Rahimi, R.; Kerdari, H.; Rabbani, M.; Shafiee, M. *Desalination* **2011**, *283*, 412.
- (250) Yan-Ping, C.; Cui-Ling, R.; Yang, Q.; Zhen-Yang, Z.; Li-Jun, D.; Xing-Guo, C. *Appl. Surf. Sci.* **2011**, *257*, 8610.
- (251) Kiani, G.; Dostali, M.; Rostami, A.; Khataee, A. R. *Appl. Clay Sci.* **2011**, *54*, 34.
- (252) Absalan, G.; Asadi, M.; Kamran, S.; Sheikhan, L.; Goltz, D. M. *J. Hazard. Mater.* **2011**, *192*, 476.
- (253) Fan, J.; Cai, W.; Yu, J. *Chem. Asian J.* **2011**, *6*, 2481.
- (254) Zhou, L.; Jin, J.; Liu, Z.; Liang, X.; Shang, C. *J. Hazard. Mater.* **2011**, *185*, 1045.
- (255) Tai, Y.; Wang, L.; Gao, J.; Amer, W. A.; Ding, W.; Yu, H. *J. Colloid Interface Sci.* **2011**, *360*, 731.
- (256) Tuutijarvi, T.; Lu, J.; Sillanpaa, M.; Chen, G. *J. Hazard. Mater.* **2009**, *166*, 1415.
- (257) Zhou, Y. T.; Nie, H. L.; White, C. B.; Hea, Z. Y.; Zhua, L. M. *J. Colloid Interface Sci.* **2009**, *330*, 29.
- (258) Uzum, C.; Shahwan, T.; Eroglu, A. E.; Lieberwirth, I.; Scott, T. B.; Halla, K. R. *Chem. Eng. J.* **2008**, *144*, 213.
- (259) Uzum, C.; Shahwan, T.; Eroglu, A. E.; Hallam, K. R.; Scott, T. B.; Lieberwirth, I. *Appl. Clay Sci.* **2009**, *43*, 172.
- (260) Wang, X.; Zhao, C.; Zhao, P.; Dou, P.; Ding, Y.; Xu, P. *Bioresour. Technol.* **2009**, *100*, 2301.