

Technologies Developing in Heavy Metals' Removal from Water

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Elevated concentrations of heavy metals in drinking water resources and industrial or urban wastewater pose a serious threat to human health and the equilibrium of ecosystems. During the last few decades, the tendency to set more strict regulations on acceptable limits by the authorities, has presented the challenge of improving conventional treatment technologies or adopting innovative processes. However, meeting the technology-based treatment standards, complying with local legislation, and keeping the designed system economically viable are not always easy tasks to fulfil. This Special Issue includes a collection of high-significance research studies presenting state of the art approaches for the selective removal of soluble forms of heavy metals and other contaminants from polluted drinking water or wastewater. Most of the papers emphasize the potential implementation of relevant technologies in large-scale facilities operating under realistic conditions of water or wastewater treatment, while cost analysis features—with respect to efficiency and alternative methods that are currently applied—are also included. In particular, chemical coagulation, electrocoagulation, adsorption and biosorption are among the developed and discussed methodologies listed in this collection.

The first category of publications consists of studies on the development of coagulation processes for the treatment of water with high concentrations of selenium, thallium or heavily polluted industrial wastewater. Fu et al. presented a study for the removal of trace thallium from real industrial wastewater using an electrocoagulation method with iron electrodes [1]. Electrocoagulation produces in situ polymeric iron hydroxyl complexes that are able to capture aqueous forms of Th by direct adsorption or electrostatic attraction followed by coagulation. In this study, a scalable aeration–forced pump cycling reaction system operating in batch mode was developed and tested in order to maximize efficiency of the electrocoagulation process. The effect of pH, dissolved oxygen, current density and initial concentration ($<165 \mu\text{g/L}$) were investigated. Alkaline conditions and good aeration were the key parameters required in order to succeed in reducing residual concentrations below the regulation limit, while ensuring minimal energy consumption. The coagulant formed consisted of iron oxy-hydroxides, with ferrihydrite sheets representing the dominant phase at high pH values. The presented system, which takes advantage of a combined electrostatic attraction and inner-sphere complex formation mechanism, can be easily converted to a continuous reaction mode.

A techno-economic evaluation on the application of iron and aluminum coagulants for the removal of tetravalent selenium at concentrations below $100 \mu\text{g/L}$ was reported by Kalaitzidou et al. [2]. A variety of coagulants were tested, including pre-hydrolyzed FeCl_3 , FeClSO_4 , pre-hydrolyzed $\text{Fe}_2(\text{SO}_4)_3$ and poly-aluminum chloride. Pre-hydrolyzed FeCl_3 was found to be the most efficient chemical reagent, providing an uptake capacity of 8.9 mg/g at pH 6 when succeeding a residual Se(IV) concentration below $10 \mu\text{g/L}$. Additionally, considering parameters such as the cost of the reagent, the quantity of the produced sludge and the energy and labor costs of each process, pre-hydrolyzed FeCl_3 was shown to be the optimum choice for large-scale Se(IV) treatment systems oriented for drinking water purification.



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Tolkou et al. investigated the performance of novel composite pre-polymerized coagulants for the treatment of high-strength industrial wastewaters, such as those created by tanneries, or by yeast production industries [3]. A single poly-aluminum-ferric-silicate-chloride (PSiFAC) coagulant and a similar coagulant combined with an anionic polyelectrolyte poly-acrylamide co-polymer were tested for their ability to reduce the chemical oxygen demand (COD), the turbidity and phosphate concentration in pre-treated aerobic and anaerobic wastewater treatment samples. The PSiFAC coagulant showed improved performance when compared to the commonly applied poly-aluminum-chloride coagulants, while the residual aluminum concentration was kept below the limit for drinking water.

A second set of published works in this Special Issue deal with the development of adsorbents that are optimized to selectively capture specific heavy metals, including hexavalent chromium, antimony, arsenic, iron and manganese. Mudzielwana et al. studied the efficiency of a modified kaolin clay featuring iron and manganese precipitates, towards capture of pentavalent arsenic species [4]. Using batch adsorption experiments, the authors examined the effect of pH, the interferences of common water ions and the kinetic behavior. A maximum adsorption capacity of 2.44 mg/g was determined under acidic conditions with the adsorption being inhibited by the presence of sulfate, chloride and nitrate anions. The uptake mechanism involves both the boundary layer, diffusion, and equilibrium adsorption.

Another kaolin-based adsorbent was evaluated by Kwakye-Awuah et al. for the adsorptive removal of iron and manganese from groundwater samples from Ghana [5]. The developed Zeolite Y was synthesized by the digestion of bauxite and kaolin under alkaline conditions, followed by calcination at high temperatures. Batch adsorption experiments indicated a removal efficiency of above 98% for both iron and manganese, reaching residual concentrations below the regulation limit for drinking water. Meanwhile, the presence of an affordable variation of quality characteristics was also observed. The mechanism of adsorption involved ion exchange and particle diffusion within the zeolite network, with the adsorbent maintaining a good efficiency even after washing and reuse cycles.

Nanosized adsorbents were also evaluated for the removal of other toxic heavy metals. Papadopoulos et al. synthesized a very efficient nanomaterial for the uptake of Cr(VI) under reliable conditions of drinking water treatment [6]. A chloride-substituted stannous oxy-hydroxide formed by skein-like spherical units was prepared in large quantities in a continuous flow reactor and then used as a filler for a typical house filter to evaluate its performance. The system was able to eliminate Cr(VI) even when extremely large initial concentrations were used, verifying the high adsorption capacity of 17.5 mg/g, while keeping the residual concentration below 10 µg/L. These results suggest that this material is a favorable option for qualification in real systems, especially when also considering its low preparation cost.

The purification of water polluted with antimony generally represents a difficult problem due to the high mobility of its pentavalent form and the low regulation limit for such a heavy metal. In another study, a nanocomposite consisting of iron oxide nanoparticles decorated with iron oxy-hydroxides was introduced as a medium to combine the reduction into the trivalent form and the sequential uptake of this specie by the iron oxy-hydroxide [7]. The capacity of around 0.5 mg/g, with respect to residual concentration below the regulation limit, was one of the best values reported for Sb(V) removal. The presence of a magnetic phase, such as magnetite, initiates the possibility for application and recovery using magnetic separation schemes.

Magnetic nanoparticles were also tested by Gallo-Cordova et al. as a Cr(VI) adsorbent [8]. The nanoparticles were produced by microwave-assisted polyol method and their surface was modified by tetraethyl orthosilicate and 3-aminopropyl triethoxysilane in order to adjust the surface charge. The nanoparticles showed a good efficiency for the removal of Cr(VI) under acidic conditions, indicating the potential for incorporation in wastewater treatment cases.

Finally, a biosorbent based on a pellicle-like biofilm-producing *Methylobacterium hispanicum* EM2 strain was studied by Jeong et al. for the treatment of lead in aqueous solutions [9]. The EM2 strain used was proven to be very resistant to high lead concentrations and provided a biosorption rate of up to 96% at pH 7 for an initial Pb(II) concentration of 10 mg/L and a biomass content of 1 g/L. The developed biosorbent appeared to be similarly efficient when applied in contaminated sewage water with the co-existence of other heavy metals.

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References

1. Fu, X.; Li, L.; Yang, G.; Xu, X.; He, L.; Zhao, Z. Removal of trace thallium from industrial wastewater by Fe⁰-electrocoagulation. *Water (Switzerland)* **2020**, *12*, 163. [[CrossRef](#)]
2. Kalaitzidou, K.; Bakouros, L.; Mitrakas, M. Techno-economic evaluation of iron and aluminum coagulants on Se(IV) removal. *Water (Switzerland)* **2020**, *12*, 672. [[CrossRef](#)]
3. Tolkou, A.K.; Zouboulis, A.I. Application of composite pre-polymerized coagulants for the treatment of high-strength industrial wastewaters. *Water (Switzerland)* **2020**, *12*, 1258. [[CrossRef](#)]
4. Mudzielwana, R.; Gitari, M.W.; Ndungu, P. Uptake of As(V) from groundwater using Fe-Mn oxides modified kaolin clay: Physicochemical characterization and adsorption data modeling. *Water (Switzerland)* **2019**, *11*, 1245. [[CrossRef](#)]
5. Kwakye-Awuah, B.; Sefa-Ntiri, B.; Von-Kiti, E.; Nkrumah, I.; Williams, C. Adsorptive removal of iron and manganese from groundwater samples in Ghana by zeolite y synthesized from bauxite and kaolin. *Water (Switzerland)* **2019**, *11*, 1912. [[CrossRef](#)]
6. Papadopoulos, G.; Asimakidou, T.; Karfaridis, D.; Kellartzis, I.; Vourlias, G.; Mitrakas, M.; Simeonidis, K. An optimized Cr(VI)-Removal system using sn-based reducing adsorbents. *Water (Switzerland)* **2019**, *11*, 2477. [[CrossRef](#)]
7. Simeonidis, K.; Kalaitzidou, K.; Kaprara, E.; Mitrika, G.; Asimakidou, T.; Balcells, L.; Mitrakas, M. Uptake of Sb(V) by nano Fe₃O₄-decorated iron oxy-hydroxides. *Water (Switzerland)* **2019**, *11*, 181. [[CrossRef](#)]
8. Gallo-Cordova, A.; Morales, M.d.P.; Mazarío, E. Effect of the surface charge on the adsorption capacity of chromium(VI) of iron oxide magnetic nanoparticles prepared by microwave-assisted synthesis. *Water (Switzerland)* **2019**, *11*, 2372. [[CrossRef](#)]
9. Jeong, S.W.; Kim, H.K.; Yang, J.E.; Choi, Y.J. Removal of Pb(II) by pellicle-like biofilm-producing *Methylobacterium hispanicum* EM2 strain from aqueous media. *Water (Switzerland)* **2019**, *11*, 2081. [[CrossRef](#)]