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Nanomaterials as Sorbents to Remove Heavy Metal Ions in Wastewater Treatment

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Abstract

Wastewater containing heavy metal ions is considered as the serious environmental problem in human society. Adsorption as the widely used method plays an important role in wastewater treatment, which is based on the physical interaction between metal ions and sorbents. With the development of nanotechnology, nanomaterials are used as the sorbents in wastewater treatment; several researches have proved that nanomaterials are the effective sorbents for the removal of heavy metal ions from wastewater due to their unique structure properties. Three kinds of nanomaterials are presented in this paper, including nanocarbon materials, nanometal particles, and polymer-supported nanoparticles. For heavy metal ions, all these nanomaterials show high selectivities and adsorption capacities. Besides, the adsorption isotherm model and adsorption kinetics are introduced briefly to understand the adsorption procedure.

Keywords: Nanomaterials; Adsorption; Heavy metal ions; Wastewater treatment

Introduction

Different contaminants are released to wastewater with the rapid industrialization of human society, including heavy metal ions, organics, bacteria, viruses, and so on, which are serious harmful to human health. Among all water contaminations, heavy metal ions, such as Pb^{2+}, Cd^{2+}, Zn^{2+}, Ni^{2+} and Hg^{2+}, have high toxic and non-biodegradable properties, can cause severe health problems in animals and human beings. It is well-known that chronic cadmium toxicity is the inducement of Japan Itai-Itai disease. The harmful effects of Cd also lead a number of acute and chronic disorders, such as renal damage, emphysema, hypertension, testicular atrophy, and skeletal malformation in fetus [1,2]. Wastewater from many industries, including chemical manufacturing, battery manufacturing industries, metallurgical, leather tanning, and mining, contain these heavy metal ions [3]. These wastewater with heavy metal ions are discharged into natural water directly, not only threat the aquatic organisms, but may be enriched by precipitation, adsorption, and harmed human health through the food chain. Thus, the removal of such toxic metal ions from wastewater is becoming a crucial issue.

Heavy metal ions could be eliminated by several traditional techniques [4], including chemical precipitation [5], reverse osmosis [6], electrochemical treatment techniques [7], ion exchange [8], membrane filtration [9], coagulation [10], extraction [11], irradiation [12], and adsorption [13]. Due to its low cost-effective, high efficiency, and simple to operate for removing trace levels of heavy metal ions, adsorption technology [14] is regarded as the most promising one to remove heavy metal ions from effluents among these techniques mentioned above. Several types of materials, such as activated carbons [15], clay minerals [16], chelating materials [17], and chitosan/natural zeolites [18] have been researched to adsorb metal ions from aqueous solutions. Although traditional sorbents could remove heavy metal ions from wastewater, the low sorption capacities and efficiencies limit their application deeply.

To solve these defects of traditional sorbents, nanomaterials are used as the novel ones to remove heavy metal ions in wastewater. Materials with the particle size between 1 nm to 100 nm are defined as nanomaterials. With novel size- and shape-dependent properties, nanomaterials have been extensively investigated over a decade [19]. In recent years, the development of nanoscience and nanotechnology has shown remarkable potential for the remediation of environmental problems [20,21]. Compared with traditional materials, nanostructure adsorbents have exhibited much higher efficiency and faster rates in water treatment.

Nanomaterials for Adsorption

Used as sorbents for removing heavy metal ions in wastewater, nanomaterials should satisfy the following criterions: 1) The nanosorbents themselves should be nontoxic. 2) The sorbents present relatively high sorption capacities and selectivity to the low concentration of pollutants. 3) The adsorbed pollutant could be removed from the surface of the nano adsorbent easily. 4) The sorbents could be infinitely recycled. So far, a variety of nanomaterials such as carbon nanotubes, carbon based material composites, graphene, nano metal or metal oxides, and polymeric sorbents have been studied in the removal of heavy metal ions from aqueous solutions, and the results indicate that these nanomaterials show high adsorption capacity.

Carbon based nanomaterials

As one of the inorganic materials, carbon based nanomaterials [22] are used widely in the field of removal heavy metals in recent decades, due to its nontoxicity and high sorption capacities. Activated carbon is used firstly as sorbents, but it is difficult to remove heavy metals at ppb levels. Then, with the development of nanotechnology, carbon nanotubes, fullerene, and graphene are synthesized and used as nanosorbents.

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Carbon nanotubes (CNTs) are discovered by Lijima, due to their unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties, have been applied widely to remove heavy metals in wastewater treatment. CNTs are used as nanosorbents separately firstly, and show high sorption efficiency of divalent metal ions. Pyrzyńska and Bystrzejewski [23] give the advantages and limitations of heavy metals sorption onto activated carbon, carbon nanotubes, and carbon-encapsulate magnetic nanoparticles, through sorption studies based on Co^{2+} and Cu^{2+}. The results show that carbon nanomaterials have significantly higher sorption efficiency comparing with activated carbons. Meanwhile, Stafiej and Pyrzynska [24] find solution conditions, including pH and metal ions concentrations, could affect the adsorption characteristics of carbon nanotubes, and the Freundlich adsorption model agree well with their experimental data.

Then, to enhance the sorption capacities, CNTs are modified by oxidation [25,26], combing with other metal ions [27] or metal oxides [28], and coupling with organic compounds [29]. Ball et al. [30] showed that carboxyl-carbon sites are over 20 times more energetic for zinc sorption than unoxidized carbon sites. Salam et al. [29] modified carbon nanotubes with 8-hydroxyquinoline, which are used to remove of Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+}. In this paper, adsorption parameters, such as the amount of carbon nanotubes used, temperature, pH, ionic strength, metal ion concentration are studied and optimized. The results show that most of the metals are removed from aqueous solution. The modification of CNTs with 8-hydroxyquinoline enhanced significantly the removal process.

Graphene is another type carbon material as nanosorbent, which is a kind of one or several atomic layered graphites, possesses special two-dimensional structure and good mechanical, thermal properties. Wang et al. [1] synthesized the few-layered graphene oxide nanosheets through the modified Hummers method, this graphene nanosheets are used as sorbents for the removal of Cd^{2+} and Co^{2+} ions from aqueous solution, results indicate that heavy metal ions sorption on nanosheets is dependent on pH and ionic strength, and the abundant oxygen-containing functional groups on the surfaces of graphene oxide nanosheets played an important role on sorption. Kim et al. [31] reported magnetite-graphene adsorbents with a particle size of ~10 nm give a high binding capacity for As^{3+} and As^{5+}, and the results indicate that the high binding capacity is due to the increased adsorption sites in the graphene composite.

Nanoparticles from metal or metal oxides

Nanoparticles formed by metal or metal oxides are another inorganic nanomaterials, which are used broadly to remove heavy metal ions in wastewater treatment. Nanosized metals or metal oxides include nanosized silver nanoparticles [32], ferric oxides [33], manganese oxides [34], titanium oxides [35], magnesium oxides [19], copper oxides [36], cerium oxides [37], and so on, all these provide high surface area and specific affinity. Besides, metal oxides possess minimal environmental impact and low solubility and no secondary pollution, have been adopted as sorbents to remove heavy metals.

Hristovski et al. [38] research the feasibility of arsenate removal by aggregated metal oxide nanoparticle media in packed bed columns. Through batch experiments conduct with 16 commercial nanopowders in four water matrices, TiO_2, Fe_2O_3, ZrO_2, and NiO nanopowders are selected out by characterized with fitted Freundlich adsorption isotherm parameters, which exhibit the highest arsenate removal in all water matrices. Cao et al. [39] synthesized the titanate nanoflowers through a facile hydrothermal treatment of anatase nanopowders in concentration NaOH solution. The nanoflowers have large specific surface area and show availability for the removal of heavy metal ions from water system. Comparative studies exhibit that titanate nanoflowers possess larger adsorption capacity and more rapid kinetics than titanate nanotubes/nanowires. Besides, Titanate nanoflowers showed high selectivity in the removal of highly toxic heavy metal ion Cd^{2+} than less toxic ions Zn^{2+}, Ni^{2+}, which are the potential adsorbents for efficient removal of toxic metal ions. The equilibrium data show the adsorption mechanism fitted well with the Langmuir model, the adsorption kinetics followed the pseudo-second-order model. In addition, nanosized metal or metal oxides can be embedded in supports. Chen et al. [40] synthesized the highly ordered $Mg(OH)_2$ nanotube arrays inside the pores of porous anodic alumina membranes to form $Mg(OH)_2/Al_2O_3$ composite membranes. And these membranes are used to remove Nickel ions from wastewater with high removal efficiency. Then, $MgO/NiO/Al_2O_3$ metal-oxides nanostructures are gained after heating the composite membranes, which still present nice performance of Ni^{2+} removal.

Nanosized metal oxides show great removal efficiency of heavy metal in wastewater, owing to their higher surface areas and much more surface active sites than bulk materials. But, it is very difficult to separate them from the wastewater due to their high surface energy and nanosize. So, many researchers turn to design polymer based nanosorbents.

Polymer supported nanosorbents

An efficient sorbent with both high capacity and fast rate adsorption should have the following two main characteristics: functional groups and large surface area [41]. Unfortunately, most current inorganic sorbents rarely have both at the same time, carbon nanomaterials has high surface area, but without adsorbing functional group. On the contrary, organic polymer, polyphenylenediamine, holds a large amount of polyfunctional groups (amino and imino groups) can effectively adsorb heavy metal ions, whereas their small specific area and low adsorption rate limit their application. Therefore, new sorbents with both polyfunctional groups and high surface area are still expected. More recently, the development of hybrid sorbents has opened up the new opportunities of their application in deep removal of heavy metals from water [42,43].

Polymer-layered silicate nanocomposites [44] have attracted both academic and industrial attention because they exhibit dramatic improvement in properties at very low filler contents. Xu et al. [45] synthesized the hybrid polymers from the ring-opening polymerization of pyromellitic acid dianhydride (PMDA) and phenylaminomethyl trimethoxysilane (PAMTMS). This hybrid polymer is used to remove Cu^{2+} and Pb^{2+}, adsorption for Cu^{2+} and Pb^{2+} followed Lagergren second-order kinetic model and Langmuir isotherm model, demonstrating that the adsorption process might be Langmuir monolayer adsorption.

In summary, nanomaterials including traditional inorganic nanoadsorbents and novel polymer supported composites are used to remove the heavy metal ions in wastewater treatment, due to their novel size- and shape-dependent properties, and gain the good to excellent removal efficiency.

Adsorption Isotherm

Adsorption is the process in which heavy metals are adsorbed on the solid surface, and the equilibrium is established when the concentrations of heavy metal adsorbed and in water become constant.

At equilibrium, the relationship between amounts of heavy metal ions adsorbed and in water is called an adsorption isotherm [21]. From these isotherms, several adsorption parameters could be calculated. The most widely used adsorption isotherms are Langmuir model and Freundlich model.

Langmuir model

In this model, adsorption occurs uniformly on the active sites of the adsorbent, and once the active sites are occupied by adsorbates, the adsorption is naturally terminated at this site. The non-linear Langmuir equation is [46,47]:

$$q = \frac{q_{\max} K_L C}{1 + K_L C} \quad (1)$$

where K_L is the equilibrium constant (L mg^{-1}), q_{max} is the maximum adsorption capacity (mg g^{-1}) of adsorbent, C is the equilibrium concentration (mg L^{-1}), q is the amount of metals adsorbed at equilibrium (mg g^{-1}).

The linear Langmuir model is given by following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (2)$$

where q_m and b are the saturated monolayer adsorption capacity and the adsorption equilibrium constant. A plot of C_e/q_e versus C_e would result in a straight line. From the slope and intercept, the maximum adsorption capacity and bond energy of adsorbates can be calculated.

Freundlich adsorption isotherm

The Freundlich equation is an empirical model allowing for multilayer adsorption on sorbent. The non-linear form of Freundlich model is [48]:

$$q_e = K_F C_e^n \quad (3)$$

The linear form of Freundlich model can be expressed as:

$$\log q_e = \log K_F + \frac{\log C_e}{n} \quad (4)$$

where q_e is loading of adsorbate on adsorbent at equilibrium (mg g^{-1}); K_F is indicator of sorption capacity (mg^{1-n} L^n g^{-1}), n is adsorption energetics and C_e is aqueous concentration of adsorbate at equilibrium (mg L^{-1}).

As the widely used models, the Langmuir model assumes monolayer coverage on sorbent whereas the Freundlich model is an empirical model allowing for multilayer adsorption on sorbent [49]. Besides, there are several different well-known models used to explain the results of adsorption studies, including Tempkin [50], Frenkel–Halsey–Hill [51], Henderson [52], Giles-Smith [53], Dubinin-Radushkevich [54], MT [55], BET [56], BDST [57], Oswin [58], Ferro-Fintan [59], GAB [60], and Peleg [61]. These adsorption models give a representation of the adsorption equilibrium between an adsorbate in solution and the surface of the adsorbent [62].

Adsorption Kinetics Model

In order to determine and interpret the mechanisms of metal adsorption processes and the main parameters governing sorption kinetics, several kinetic models are proposed.

Pseudo-first-order kinetics model

A simple kinetic model suggested for the sorption process in solid/liquid systems is Lagergren's pseudo-first-order expression, which is given as [63]:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (5)$$

Where k_1 is the pseudo-first-order rate constant for the adsorption process (min^{-1}), q_e and q_t are the amounts of metal ions adsorbed per gram of sorbents (mg g^{-1}) at equilibrium and at time t (min), respectively. After integration of this kinetic expression for the initial condition of q_t equal to 0, when time (t) approaches 0, its linear form are obtained:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

The plot of $\ln(q_e\text{-}q_t)$ vs t gives a straight line, and pseudo- first-order rate constant k_1 can be calculated from the slope of that line.

Pseudo-second-order kinetics model

The kinetic data also can be analyzed by Ho's pseudo-second-order kinetics model. This model is based on the assumption the sorption follows second order chemisorptions, which can be represented in the linear expression as [64]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where k_2 ($g{\cdot}mg^{-1}{\cdot}min^{-1}$) is the rate constant of the pseudo-second-order adsorption.

Besides two kinetic models mentioned above, researchers also propose other models, e.g. Elovich equation [65], Weber-Morris diffusion model [66], and so on.

Conclusion

Advances in nanoscale science and engineering are providing new opportunities to develop more cost-effective and environmentally acceptable water treatment technology. Nanomaterials have a number of physicochemical properties that make them particularly attractive for wastewater purification. Recent researches have indicated that nanomaterials as sorbents are useful tools for heavy metal removal, due to their unique structure and surface characteristics. These materials are capable to remove heavy metal ions at low concentration, with high selectivity and adsorption capacity. These properties of nanosorbents make them ideal materials for wastewater treatment technology. To explain the mechanism of adsorption process, adsorption isotherm and adsorption kinetics are concluded in this paper. Although nanosorbents, such as CNTs, nanometal or nanometal oxides, and other organic sorbents, are used successfully in removal heavy metal ions in wastewater, it still remains several problems; wastewater treatment on a large scale is the essential one. Besides, to develop some environment friendly and inexpensive nanomaterials is also the key work. With the nanotechnology developed, the exploitation of new efficient adsorption materials is essential and will continue infinitely, the future of nanomaterials in removal heavy metal ions in wastewater treatment is fairly bright.

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