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Review

Adsorption of heavy metals on conventional and nanostructured materials for wastewater treatment purposes: A review

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ABSTRACT

The problem of water pollution is of a great concern. Adsorption is one of the most efficient techniques for removing noxious heavy metals from the solvent phase. This paper presents a detailed information and review on the adsorption of noxious heavy metal ions from wastewater effluents using various adsorbents – i.e., conventional (activated carbons, zeolites, clays, biosorbents, and industrial by-products) and nanostructured (fullerenes, carbon nanotubes, graphenes). In addition to this, the efficiency of developed materials for adsorption of the heavy metals is discussed in detail along with the comparison of their maximum adsorption capacity in tabular form. A special focus is made on the perspectives of further wider applications of nanostructured adsorbents (especially, carbon nanotubes and graphenes) in wastewater treatment.

1. Introduction

Rational use of water resources appears to be one of the world's urgent environmental problems, the solution to which largely lies in treating wastewater that comes from human activities in various fields: industries (such as metallurgical, mining, chemical, tannery, battery and nuclear), agriculture, shipping and others. It is especially important to control contents of heavy metals (Roccaro et al., 2013; Ariffin et al., 2017) which are one of the most biologically dangerous and toxic components of wastewater effluents. Heavy metals are the group of trace elements i.e. metals and metalloids with an atomic density greater than 4 ± 1 g/cm^3, e.g., Cu, Zn, Hg, Cd, Pb, Sn, Fe, Mn, Ag, Cr, Co, Ni, As, Al etc. These metal ions are generally considered as the most widespread toxic mineral contaminants of soil and water systems (Salem et al., 2000; Mohammed et al., 2011).

There are two main sources of heavy metals in wastewater effluents viz. natural and anthropogenic. The former includes soil erosion, volcanic activities, weathering of rocks and minerals, whereas the later comprises mineral processing, fuel combustion, street run-offs, landfills, agricultural activities, and industrial activities (mining, printed board manufacturing, metal finishing and plating, semiconductor manufacturing, textile dyes, etc). Due to stability, high solubility and migration activity of heavy metals in aqueous media, untreated or inadequately treated metal-contaminated wastewater effluents cause a variety of health and environmental impacts when released into water bodies (Akpor et al., 2014).

Heavy metals are absorbed by plants, thereby entering the animal and human bodies through food chains and negatively affecting their health and vital activity (Baldwin and Marshall, 1999; Barakat, 2011; Akpor et al., 2014; Harvey et al., 2015). Table 1 demonstrates the negative effects on human health caused by the most hazardous heavy metals (As, Cd, Cr, Cu, Hg, Ni, Pb, and Zn) and the maximum contaminant level (MCL) standards in drinking water set by the US Environmental Protection Agency (US EPA) for these contaminants. The structure of atom electron shells of these contaminants determines their high reactivity, tendency to form complexes and, consequently, high biochemical and physiological activity, thereby leading to several environmental and health impacts. Therefore, it is necessary to treat heavy metal-contaminated wastewater prior to its discharge to the environment in order to avoid negative consequences such as getting into drinking water.

Heavy metals can be removed from aqueous media using various conventional methods such as chemical precipitation, solvent extraction, membrane filtration, ion exchange, electrochemical removal, coagulation etc. However, these techniques have some disadvantages such as incomplete removal, high-energy requirements and availability of toxic sludge, low efficiency, sensitive operating conditions and costly disposal (Eccles, 1999; Barakat, 2011).

To overcome these drawbacks, many approaches aimed at developing cheaper and more efficient methods to improve the quality of

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Table 1
MCL standards and ill effects of hazardous heavy metals (Babel and Kurniawan, 2003).

Heavy metal	Ill effects	MCL, mg/L
As	Skin and vascular diseases, visceral cancer	0.05
Cd	Renal disorders and damage, Carcinogenic	0.01
Cr	Headache, Diarrhea, Nausea, Carcinogenic	0.05
Cu	Liver damage, Wilson's disease, Insomnia	0.25
Hg	Rheumatoid arthritis, Circulatory & Nervous disorders	3.0×10^{-5}
Ni	Dermatitis, Chronic Asthma, Carcinogenic	0.20
Pb	Cerebral disorders, Renal, Circulatory & Nervous disorders	6.0×10^{-3}
Zn	Depression, lethargy, neurological signs, increased thirst	0.80

treated effluents have been proposed. The majority of them are based on using adsorption processes, since adsorption appears to have the greatest impact on transport, toxicity and biological availability of heavy metals (especially, at their trace amounts) in aqueous media besides, it is easy to operate and cost effective (Leung et al., 2000; Coelho et al., 2014; Santhosh et al., 2016).

Adsorption is often accompanied with the inverse process – desorption, which represents the transfer of adsorbate ions from the adsorbent surface to the solution. Depending on the adsorbate amount desorbed from the adsorbent, one can judge on the reversibility of adsorption: the more adsorbate is desorbed, the more reversible the adsorption process is (Mishra, 2014).

There are two types of adsorption – physical, in which the increase in the adsorbate concentration at the interface is due to non-specific (i.e., not dependent on the substance nature) van der Waals forces, and chemical (chemisorption) caused by chemical reactions between the adsorbate and the adsorbent which create covalent or ionic bonds. Physical adsorption is weakly specific, reversible, its thermal effect is small (units of kJ/mol), whereas chemisorption is selective, usually irreversible, its heat ranges from tens to hundreds of kJ/mol (Gupta et al., 2015; Tripathi and Ranjan, 2015; Singh and Gupta, 2016).

Nowadays, adsorption is considered as an efficient and low-cost technique for removing noxious heavy metal ions from wastewater effluents. This process is flexible in design and operation and allows for producing high-quality treated effluents. Furthermore, since the adsorption is reversible in some cases, adsorbents can be regenerated through desorption (Fu and Wang, 2011).

There are many factors which affect the efficiency of adsorbents for heavy metal removal from wastewater: e.g., initial concentration, temperature, adsorbent dose, pH, contact time, and stirring speed. The percentage (rate) of heavy metal adsorption usually increases with increase in the above-mentioned factors (Sahu et al., 2009; Bisht et al., 2016).

The adsorption of heavy metals can be described by the commonly used Langmuir or Freundlich isotherm models. The Freundlich equation is often useful for modeling sorption of metals onto solids with heterogeneous surfaces and has frequently proved superior to the Langmuir equation for the adsorption of cations such as heavy metals. Although there is a disagreement regarding the effectiveness of the Langmuir and Freundlich models in interpreting the metal adsorption, some parameters of these models, such as the Langmuir maximum adsorption capacity (q_{max}) and the Freundlich constant related to the distribution coefficient (K_F), are widely acceptable in characterizing the metal sorption capacity of various materials (Shaheen at al, 2012).

Materials used as adsorbents should have a high adsorption interaction towards the target contaminants in order to effectively remove them from wastewater effluents. The adsorbents may be of mineral, organic or biological origin – e.g., activated carbons, zeolites, clay minerals, industrial by-products, agricultural waste, biomass, and polymeric materials (Kurniawan et al., 2005; Barakat, 2011; Gautam et al., 2014).

Over the past twenty years, nanotechnology has been applied in almost all branches of science and technology. As a matter of fact, different materials based on carbon nanostructures such as fullerenes, carbon nanotubes, graphene and graphene oxide have been synthesized and used to remove the contaminants considered herein from aquatic (Rao et al., 2007; Gupta and Saleh, 2013; Gautam and Chattopadhyaya, 2016; Santhosh et al., 2016). Taking into account the importance of water quality and emerging benefits of nanotechnology, attempts have been made to discuss various issues of water treatment using nanoadsorbents. In this regard, such nanomaterials may present opportunities for elaborating perspective solutions to the water pollution problem.

Considering the aforementioned, the present paper contains a review on the use of various types of materials i.e. conventional and nanostructured as adsorbents for removing heavy metals from wastewater effluents. Besides, a comparison of these materials regarding the adsorption capacity for the considered contaminants is provided, with a conclusion on perspectives of employing nanomodified adsorbents.

2. Adsorption removal of heavy metals from wastewater

Adsorption (in the case considered in the present review) is the process taking place when a liquid solute (adsorbate) accumulates on the surface of a solid (adsorbent) and forms a molecular or atomic film.

2.1. Adsorption on conventional materials

There exist numerous adsorbents of different nature and they can be employed in initial or modified forms for removing noxious heavy metals ions from wastewater effluents. The most frequently used ones are activated carbons, zeolites, clay minerals, industrial solid waste, and biomaterials (Singh and Gupta, 2016). Some of them are described below.

2.1.1. Activated carbons and agricultural waste on the basis thereof

Adsorbents based on activated carbons (ACs) are widely used to remove heavy metal contaminants due to their well-developed porous structure (large mesopores and micropore volumes) and a high specific surface area, as well as different surface functional groups (including carboxyl, carbonyl, phenol, quinone, lactone, and others) bound to the edges of the graphite-like layers. The most widely used carbonaceous materials for the AC industrial production are coal, wood and coconut shell (Jusoh et al., 2007; Kang et al., 2008; Fu and Wang, 2011; Deliyanni et al., 2015).

Since coal-based ACs are expensive, their use has been limited nowadays, and further efforts have been made to convert cheap and abundant sources into ACs (Anirudhan and Sreekumari, 2011). In this regard, ACs can be prepared from various agricultural waste.

Kongsuwan et al. (2009) explored the use of AC from eucalyptus bark in the binary component sorption of Cu^{2+} and Pb^{2+}. The maximum adsorption capacity for Cu^{2+} and Pb^{2+} was 0.45 and 0.53 mmol/g, respectively, and adsorption was found to be the major mechanism for the uptake of both heavy metals. Poultry litter to manufacture AC for treating heavy metal-contaminated water was investigated by Guo et al. (2010). They revealed that poultry litter-based AC possesses a significantly higher adsorption affinity and capacity for heavy metals than commercial AC derived from bituminous coal and coconut shell.

Karthikeyan et al. (2005) removed Cr^{6+} from wastewater using AC derived from rubber wood saw dust. They achieved the maximum adsorption capacity of 44 mg/g at the optimum pH 2.0, which was higher as compared to the other adsorbents such as coconut tree saw dust (Selvi et al., 2001), coconut shell carbon (Babel and Kurniawan, 2004), sugarcane bagasse (Sharma and Forster, 1994), and treated saw dust of Indian rose wood (Garg et al., 2004), where the Cr^{6+} maximum adsorption capacity was found to be only 3.60, 10.88, 13.40, and 10 mg/g, respectively. Lo et al. (2012)derived AC from Moso and Ma bamboo