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Heavy metals removal from aqueous solutions and wastewaters by using various byproducts

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ABSTRACT

Water contamination with heavy metals (HM) represents a potential threat to humans, animals and plants, and thus removal of these metals from contaminated waters has received increasing attention. The present study aimed to assess the efficiency of some low cost sorbents i.e., chitosan (CH), egg shell (ES), humate potassium (HK), and sugar beet factory lime (SBFL) for removal of cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) from wastewaters. For this purpose batch equilibrium experiments were conducted with aqueous solutions containing various concentrations of the metals and sorbents in a mono-metal and competitive sorption system. Sorption isotherms were developed, and sorption parameters were determined. The potential applicability of the tested sorbents in the removal of Cd, Cu, and Zn from contaminated wastewaters was also investigated by equilibrating different sorbents and water ratios.

Chitosan expressed the highest affinity for the metals followed by SBFL, ES, and HK. Nearly 100% of the metals were removed from aqueous solutions with the lowest initial metal concentrations by the sorbents especially CH and SBFL. However, the sorption efficiency decreased as the initial metal concentrations increased. Competition among the four metals changed significantly their distribution coefficient (K_d) values with the sorbents. The selectivity sequence of the metals was: Pb > Cu > Zn > Cd. The metal removal from the wastewaters varied from 72, 69, and 60 to nearly 100% for Cd, Cu and Zn, respectively. The efficiency of the studied byproducts in removing metals from the wastewaters differed based on the source of contamination and metal concentrations. Cadmium removal percentages by HK and CH were higher than SBFL and ES. The HK and CH exhibited the highest removal percentage of Cu from water with high concentrations. The SBFL and ES revealed the highest removal percentage of Zn from water with high concentrations. The results, demonstrate a high potential of CH, SBFL, HK, and ES for the remediation of HM contaminated wastewaters.

1. Introduction

Contamination of waters by heavy metals (HM) through the discharge of industrial wastewater is a worldwide environmental problem. Rapid industrialization has seriously contributed to the release of potentially toxic HM to water streams. Lead (Pb), copper (Cu), cadmium (Cd), and zinc (Zn) are among the most common metals found in industrial effluents (Ahmaruzzaman, 2011). Environmental contamination with HM represents a potential threat to humans, animals and plants (Kim et al., 2012). Thus, the removal of HM from contaminated wastewater has received increasing attention (Fu and Wang, 2011). Additionally, remediation of HM contaminated waters using some environmental friendly and low cost sorbents is a potentially applicable option (Aydin et al., 2008). The increasing demand for new and costly processes for the recovery of metal from industrial effluents has led many researchers to investigate the possibility of using waste biomaterials for metal sorption. Recently many studies have focused on the development of non-conventional alternative sorbents produced from renewable and low-cost resources which can be used for the removal of metal from different aqueous solutions and wastewaters (Gupta et al., 2009). Some of these materials exhibit high sorption capacity and differ from the traditional synthetic ion exchangers since they are biodegradable, cheap and come from renewable sources (Sdiri

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et al., 2012). The main advantages gained by using biomass as a biosorbent and/or alternative sorbent, i.e., it is environmentally friendly (waste for waste treatment), locally available in large amounts, low economic value, and attached metals can be easily recovered while biosorbent may be reusable (Babel and Kurniawan, 2003; Lesmana et al., 2009). After remediation, options for resultant sludge treatment include landfilling, incineration, stabilization and cement-based solidification (Skrypski-Mäntele et al., 2000). The application of chemical extraction, supercritical fluid extraction, bioleaching and electrokinetic process in removing metals from contaminated sludge have been considered (Babel and del Mundo Dacera, 2006). Furthermore, conversion of sludge into activated carbon, would improve economic value, and help industries reduce the cost of waste disposal by landfills and incineration (Kurniawan et al., 2006).

One of the low-cost sorbents is chitosan (CH). Chitosan is obtained on an industrial scale by the alkaline deacetylation of chitin, one of the most abundant biopolymers in nature. The ability of CH to form complexes with metal ions is well documented (e.g., Rangel-Mendez et al., 2009; Kamari et al., 2011). Most of the previous studies have dealt with examining the capability of CH to adsorb metal ions from solutions containing a single solute. However, wastewaters usually contain a mixture of metals exhibiting a different sorption pattern than that of a single metal. So far, no attempts have been made to examine sorption mechanisms of CH in the presence of more than one metal in water solutions or contaminated wastewaters.

Sugar beet factories have traditionally stockpiled factory lime near them which is produced during the sugar beet juice purification process. This factory lime meets the definition of a liming product and can be used for remediation of metal contaminated soils and waters (Dutton and Huijbregts, 2006). Removal of potentially toxic metals by using natural limestone has been investigated by several researchers (e.g., Aziz et al., 2008; Sdiri et al., 2012). However, the efficiency of limestone in removal of metals is usually low for intensive remediation operations. Sugar beet factory lime due to its alkalinity and finer texture is expected to be more efficient in HM sorption compared to limestone. Additionally, to our knowledge, no attempt has been made to assess the effects of SBFL instead of the natural limestone to remove metals either from aqueous solution or contaminated wastewaters.

In Egypt, domestic egg consumption is high and continues to increase with the rapid increase of population. Egg consumption generates big quantities of ES waste every year. Waste ES contain high amounts of calcium carbonate (85–95%). Ok et al. (2011) reported that lime based waste materials such as egg and oyster shells can be used as an alternative to $CaCO_3$ for the immobilization of metals in contaminated soils. However, little is known about the use of ES to remove metals from aqueous solutions (Park et al., 2007; Ahmad et al., 2012).

In Egypt, rapid industrialization has seriously contributed to the release of toxic metals to drainage water streams and to the Nile River and its tributaries (Shaheen and Tsadilas, 2009). Dyeing, textile, and phosphates fertilizers industries are the main sources of such water pollution. For proper evaluation of the environmental threat posed by toxic metals, it is necessary to study their sorption characteristics not only under mono-metal but also under competitive systems since they are usually present in wastewaters as mixture. Therefore, this study was conducted to examine the effectiveness of some low cost sorbents in removal of Cd, Cu, Pb, and Zn under competitive system either in artificially contaminated aqueous solutions or wastewaters. The present study was undertaken to test how the competitive sorption of poorly sorbed trace elements (Cd and Zn) and strongly sorbed metals (Pb and Cu) affects their behavior in sorbents with large variation in types and properties. Therefore, the objective of this study was to assess the sorption behavior of four divalent metals (Cd, Cu, Pb, and Zn) onto four locally derived sorbents, namely chitosan, eggshell, humate potassium, and sugar beet factory lime, in a mono-metal and competitive sorption system. The potential applicability of the tested sorbents in the removal of Cd, Cu and Zn from contaminated industrial wastewater was also investigated.

2. Materials and methods

2.1. Selection and characterization of studied sorbents

The CH was obtained from the Egyptian Petroleum research institute and was prepared as follows: The shrimp shells were deproteinized with 3.5% (w/w) NaOH solution for 2 h at 65 °C, demineralized with 1 N HCl for 1 day at ambient temperature, decolorized with acetone for 2 h at 50 °C, and dried for 2 h at ambient temperature. The removal of acetyl groups from the prepared chitin was achieved by mixing with NaOH (50%) with stirring for 2 h at 115 °C in a solid to solvent ratio of 1:10 (w/v). The resulting CH was washed till neutrality in running tap water, rinsed with distilled water, filtered, and then dried at 60 °C for 24 h (Hefni, 2010). Waste ES were collected and washed with tap water several times, air-dried and incubated in hot air oven at 40 °C for 30 min. Egg shells were ground and sieved using a 2 mm sieve. The commercial Hiuminova (HA) was used in this study. It is a water soluble humate potassium crystal contains 10% K_2O. The SBFL was obtained from the Delta sugar beet factory in El-Hamoul, Kafr El-Sheikh governorate, Egypt. Sorbent samples were air-dried and analyzed for their basic chemical properties and metals content. Sorbent pH was measured in deionized water. Total calcium carbonates equivalent were determined by using Collins calcimeter. For the total metal concentrations the samples were digested with aqua regia (DIN ISO 11466, 1997). Metal concentrations in the studied sorbents were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Ultima 2, Horiba Scientific, Unterhaching, Germany). The basic characteristics and metal concentrations in the amendments used in this study are presented in Table 1.

2.2. Collection and characterization of contaminated wastewater

Heavy metals contaminated wastewater samples were taken from three different locations of industrial wastewater: 1 – Dyeing

Table 1
Selected characteristics and total metal concentrations in the sorbents.

	CH	ES	HK	SBFL
pH	8.50	8.42	8.76	12.59
Total $CaCO_3$, %	nd	96.06	1.11	81.56
Total metal concentrations, mg kg^{-1}				
Al	204.9	nd	1894.9	1705.2
As	0.14	nd	2.19	1.61
Cd	nd	nd	nd	0.13
Co	1.82	nd	0.58	1.74
Cu	51.1	nd	nd	11.93
Ni	28.2	nd	2.68	36.04
Fe	1284.3	1.8	775.2	849.2
Hg	nd	nd	nd	nd
Mn	70.75	0.83	5.66	84.09
Mo	nd	0.55	0.28	2.12
Pb	0.50	nd	0.52	nd
S	136.4	120.2	4895.4	2025.1
Se	0.36	1.96	1.57	3.21
V	0.34	1.98	1.14	5.09
Zn	5.14	0.29	3.41	14.32

CH: chitosan; ES: egg shell; HK: humate potassium; SBFL: sugar beet factory lime. nd: not detected.