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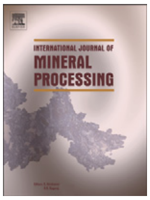

Adsorption of Pb(II), Cr(III) and Cr(VI) from aqueous solution by surfactant-modified diatomaceous earth: Equilibrium, kinetic and thermodynamic modeling studies

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ABSTRACT

The adsorption of Cr(III), Cr(VI) and Pb(II), ions onto natural (DAT) and organomodified (DAT-HDTMABR) diatomaceous earth from aqueous solutions was studied in a batch adsorption system. Factors influencing Pb(II), Cr(III) and Cr(VI) adsorption such as initial metal ion concentration (10–200 mg/L), adsorbent dosage (0.01–0.30 g/50 mL), pH (1.0–8.0), contact time (10–260 min), ionic strength (0.01–0.20 M) and temperature (25, 35 and 45 °C) were investigated. The adsorption process was relatively fast and equilibrium was established within 180 min for DAT and 120 min for DAT-HDTMABR. Maximum adsorption of Pb(II), Cr(III) and Cr(VI) was observed at pH 5, 4.5 and 2, respectively. Thus, pH 4.5 value was used throughout the whole experiments. The adsorption characteristics of the two adsorbents were generally very similar. The adsorption data obtained was well described by Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models. The maximum metal adsorption capacities assumed by a Langmuir model were on the order of $Pb^{2+} > Cr^{3+} > Cr^{6+}$. +. Adsorption energy ($E$) for adsorption of Cr(III), Cr(VI) and Pb(II) species by DAT and DAT-HDTMABR has been computed from the D–R equation. Adsorption energy evaluated for the adsorption of those three metal cations showed that an ion-exchange mechanism (physisorption) was operative. A comparison of the kinetic models on the overall adsorption rate showed that the adsorption system can be best described by the pseudo-second-order kinetics. Different thermodynamic parameters viz., Gibbs free energy ΔG, enthalpy, ΔH, entropy, ΔS, activation energy, Ea, and sticking probability, S^* have also been evaluated, and the adsorption was feasible, spontaneous, and exothermic in nature.

1. Introduction

Pollution by inorganic pollutants, in particular heavy metals is one of the most serious environmental problems faced by life and earth; they are stable and persistent environmental pollutants since they cannot be degraded or destroyed. Because of this, the concentration of these heavy metals must be reduced to the maximum permissible concentration (Oliveira et al., 2007; Lacin et al., 2005; Ayari et al., 2007).

Most heavy metals are known to be toxic and carcinogenic agents and, when discharged in wastewater, represent a serious threat to the human population. Lead and chromium are regarded as major contaminants. Lead is well recognized as an environmental pollutant that acts as a cumulative poison (Kadirvelu et al., 2007; Shin and Kim, 2014; Sari et al., 2007; Uluozlu et al., 2008; Lelli et al., 2014).

Lead and its compounds play an important role in industrial activities including the manufacture of paint and pigments, Pb-containing pesticides, battery industries and lead smelters. Lead can also enter waste waters via leaching from lead pipes and Pb/Sn-soldered joints and from runoff from land close to heavy-traffic highways (Shotyk and LeRoux, 2005; Jiang et al., 2009).

Limit values of lead in drinking water and surface water intended for drinking, as set by EU, USEPA and WHO are 10, 50 and 10 μg/L, respectively (Al-Haidary et al., 2011). However, more recently an EPA document prescribes a zero lead value in national primary drinking water standard (Abdulla et al., 2012).

Lead is known to damage the kidney, liver, basic cellular processes and brain functions. The toxic symptoms are anemia, insomnia, headache, dizziness and irritability, weakness of muscles, hallucination and renal damage (Unuabonah et al., 2008; Unuabonaha et al., 2007).

Chromium in the aquatic environment has been classified in the United State Environmental Protection Agency (USEPA) group A of human carcinogens (Costa, 2003). Chromium is introduced to aquatic system by many human activities; the major one is leather tanning. Effluents from electroplating, metal finishing, magnetic tapes, pigments, chromium mining and milling, brass, electrical and electronic equipments manufacturer and catalysis are other chromium pollution sources (Singh et al., 2001; Jacques et al., 2007). Among the several

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oxidation states (e.g., divalent, trivalent, pentavalent, and hexavalent) trivalent (Cr^{3+} and $CrOH^{2+}$) and hexavalent ($HCrO_4^-$ and $Cr_2O_7^{2-}$) species of chromium are mainly found in these industrial effluents. Cr^{6+} is known to be very toxic to both plants and animals, because it is strong oxidizing agent and a potential carcinogen (Wang et al., 2013). Although small amounts of Cr(III) is known to be essential for human in glucose metabolism, higher amounts may cause poisoning symptoms, such as allergic skin reactions (Iftikhar et al., 2009; Pan et al., 2013). USEPA has reported that the maximum level of chromium in drinking water should not exceed 0.1 mg/L (Lazaridis and Asouhidou, 2003), although the World Health Organization sets the upper limit at 0.01 mg/L (Péraz et al., 2009).

The elimination of lead and chromium from wastewater is therefore a priority concern. The conventional methods for the removal of lead and chromium and other heavy metals from water and wastewater include chemical precipitation, ionic exchange, filtration, electrochemical treatment, membrane techniques and recovery by evaporation (Gupta and Rastogi, 2009; Tiravanti et al., 1997; Kula et al., 2008; Gupta et al., 2005). All these methods are in this case either economically unfavorable or technically complicated and thus used only in special cases. Among these techniques, adsorption offers flexibility in design and operation and, in many cases it will generate high-quality treated effluent. In addition, owing to the reversible nature of most adsorption process, the adsorbents can be regenerated by suitable desorption processes for multiple use, and many desorption processes are low maintenance cost, high efficiency and ease operation. Therefore, adsorption is considered to be a particularly competitive and effective process for the removal of trace quantities of heavy metals (Hua et al., 2012; Zhou and Haynes, 2011).

Diatomite has already been used for the adsorption of different heavy metals from water and wastewaters, either in its natural form (raw) or modified (chemically or thermally), presenting very promising and positive results (Al-Ghouti et al., 2004; Al-Degs et al., 2001; Wu et al., 2005; Galal and Bakr, 2010; Song and Tu, 2012; Zaitoon et al., 2011; Musleh, 2012).

Recently, the raw and organomodified diatomaceous earth was used as adsorbent for the three nitrophenol isomers and chromium, copper, cadmium and lead ions (Al Bakain et al., to be published; Al-Karam et al., 2012). In this work, raw and organomodified diatomaceous earth was evaluated for its ability to remove Cr(III), Cr(VI) and Pb(II) from aqueous solutions through adsorption. The influence of parameters, such as adsorbent dosage, contact time, pH in the solution, ionic strength, and temperatures on the adsorption process was investigated. Various kinetic and isotherm parameters were also evaluated from batch adsorption assays.

2. Materials and methods

2.1. Instrumentation

Chromium (III), chromium (VI) and lead (II) analyses were carried out using Flame Atomic Absorption Spectrometer (FAAS) type Perkin-Elmer 400 (UK) using air and acetylene as flame gases. The instrument was calibrated using standard solutions of the metal cations investigated. A temperature-controlled JSSB-30T shaker and an mLw T5 centrifuge were used in all adsorption experiments and pH adjustment was performed in WTW inoLab model pH meter.

2.2. Chemicals

Lead (II) nitrate, $Pb(NO_3)$, chromium (III) sulfate, $Cr_2(SO_4)_3$, and potassium dichromate, $K_2Cr_2O_7$ were used in adsorption experiments. All these chemicals were obtained from Aldrich-Sigma chemical company and their purity is higher than 99% and used without further purification.

2.3. Adsorbents

The physicochemical parameters of both organomodified (DAT-HDTMABr) and unmodified (DAT) diatomaceous earth clay used for this study are given in the previous publication (Al Bakain et al., to be published). The BET specific surface area of unmodified and organomodified diatomaceous earth was measured to be 49.78 and 23.71 $m^2\,g^{-1}$ respectively, from N_2 sorption isotherms with sorptiometer (Micrometrics Gemini (V) (U.S.A.) apparatus). The cation exchange capacity (CEC) of DAT was estimated using the ethylenediamine copper complex method and the calculated value was found to be 79 meq/100 g diatomaceous earth.

2.4. General procedures

In the present investigation the batch mode of operation was selected in order to measure the progress of adsorption. 1000 mg/L of Pb (II), Cr(III) and Cr(VI) stock solution was prepared by dissolving appropriate weight of $Pb(NO_3)$, $Cr_2(SO_4)_3$ and of $K_2Cr_2O_7$ respectively, in 100 mL of deionized distilled water and dilution quantitatively to 1000 mL using deionized distilled water. Sodium chloride was employed as a background electrolyte to investigate the effect of ionic strength on the uptake of Cr(III), Cr(VI) and Pb(II).

Batch experiment was carried out by shaking adsorbent with 50 mL aqueous solution of Cr(III), Cr(VI) and Pb(II) to determine the effects of various process parameters, different conditions of pH (from 1.0 to 8.0), biosorbent dose (0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.25, and 0.30 g/50 mL), contact time (10–260 min), ionic strength (0.01, 0.05, 0.10, 0.15 and 0.20 M) and temperature (25, 35, 45 °C). Initial metal concentration (10, 20, 30, 40, 50, 60 70, 80, 90, 100, 120, 140, 160, 180 and 200 mg/L) was prepared by proper dilution from stock 1000 mg/L Cr(III), Cr(VI) and Pb(II) standard, and pH of the solution was monitored by adding 0.1 M HCl and 0.1 M NaOH solution as required. Constant amount (0.2 g/50 mL) of adsorbent was then added and content in the flask was shaken for the desired contact time in an electrically thermostated reciprocating shaker at 350 rpm. The time required for reaching equilibrium condition estimated by drawing samples at regular interval of time till the equilibrium was reached. The content of flask separated from adsorbent by a centrifuge at 3500 rpm and supernatant liquid was analyzed for remaining Cr(III), Cr(VI) and Pb(II) concentration in the sample.

The metal uptake capacity was calculated by the simple concentration difference method. The metal uptake q_e (mg metal adsorbed/g adsorbent) was calculated from the mass balance equation as follows:

$$q_e = \frac{(c_i - c_{eq})v}{m} \tag{1}$$

where C_i is the initial concentration (mg/L); C_{eq} is the equilibrium concentration (mg/L) of the metal ion in the aqueous phase; v is the volume of solution (L) and m is the mass of the adsorbent (g).

The percentage removal (% R) of Pb(II), Cr(III) and Cr(VI) was calculated as follows:

$$\%R = \frac{(C_i - C_{eq})}{C_i} \times 100. \tag{2}$$

All data represent the mean of three independent experiments.

3. Results and discussion

3.1. Effect of adsorbent dose

The dependence of Cr (III), Cr(VI) and Pb(II) on dose was studied by varying the amount of DAT and DAT-HDTMABr (0.01, 0.02, 0.04, 0.06, 0.08, 0.10, 0.15, 0.20, 0.25, and 0.30 g/50 mL) in an aqueous system