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Uptake of Cr^{3+} from aqueous solution by lignite-based humic acids

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Abstract

Humic acid (HA) produced from brown coal, a relatively abundant and inexpensive material is currently being investigated as an adsorbent to remove toxic metals from aqueous solution. The influence of five parameters (contact time, solution pH, initial metal concentration, temperature and amount of adsorbent) on the removal at 20 ± 1 °C was studied. HAs were prepared from lignites by using alkaline extraction, sedimentation and acidic precipitation. Adsorption equilibrium was achieved in about 60 min for Cr^{3+} ion. The Langmuir adsorption isotherm was used to describe observed sorption phenomena. The maximum adsorption capacity of 0.17 mmol for Ilgın (HA_1), 0.29 mmol for Beysehir (HA_2) and 0.18 mmol Ermenek (HA_3) and 0.17 mmol of Cr^{3+}/g for activated carbon (AC) was achieved, respectively at pH of 4.1. More than 84% of Cr^{3+} was removed by HA_2, 54% by HA_3 and 51% by HA_1 and 50% by AC from aqueous solution. The adsorption was strongly dependent on pH but independent of ionic strength and metal ions. The adsorption of Cr^{3+} was higher between pH 4.1 and 5.1 for all HAs and maximum sorption was observed at pH 4.1. The rise in temperature caused a slight decrease in the value of the equilibrium constant (K_c) for the sorption of Cr^{3+} ion. Complex mechanisms including ion exchange, complexation and adsorption and size exclusion are possible for sorption of Cr^{3+} ion on HAs.

Keywords: Humic acid; Chromium; Adsorption; Natural product

1. Introduction

Environmental contamination with heavy metals represents a potential threat to humans, animals and plants. The metals do not undergo biodegradation and many of them are soluble in aqueous solution, therefore become more available for living systems and accumulate in the environment. Chromium compounds are essential to many industries. Their applications include metal finishing, electroplating, leather tanning, pigments, magnetic tapes, and photography. For all of these industries, chromium in their wastewater is a major environmental problem. The control of the chromium level in wastewater is essential. The environmental protection agency (EPA) (Lalvani et al., 1998; Lalvani et al., 2000) regulates the chromium release into the environment.

HA plays an important role in controlling the behaviour and mobility of metals in the environment. It is chemically a very complex material, the structure and reactions of which are not fully understood.

They contain a variety of functional groups, which may react with metal ions. The formation process of humic acids in coal resides in the oxidation of coal mass, while the efficiency of the process depends on the type of coal, conditions of oxidation. Lignites (low-rank coals subjected to the least amount of metamorphic change during the coal-forming process) are characterized by their high oxygen and moisture contents, and contain less carbon than other higher-ranking coals, such as bituminous and anthracite (Turčániová et al., 2000).

Humus is a complex aggregate of brown- to dark-colored amorphous substances, which originated during the decomposition of plant and animal residues by microorganisms under aerobic and anaerobic conditions, usually in soils, composts, peat bogs, and water basins. Chemically,

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humus consists of certain constituents of the original plant material resistant to further decomposition either by processes of hydrolysis or by oxidation and reduction; and of various compounds synthesized by microorganisms. The mechanism of coal formation, through the peat state, is commonly explained as follows: Peat changes first to lignite, the latter to bituminous coal, and then to anthracite, through the action of heat, because of which fractional distillation takes place. The brown coal or lignites differ considerably in mode of occurrence and in their physical and chemical properties, thus the variations in the amount for HAs have been found in different deposits. Phenolic structures in HAs may be occurred from lignin in the lignocellulosic materials. HAs entering the plants at early stages of development are a supplementary source of polyphenols, which function as respiratory catalysts. This results in an increase in the living activity of the plant: enzyme systems are intensived, cell division is accelerated, root systems show greater development, and, ultimately, the yield of dry matter increases. HAs are thought to be complex aromatic macromolecules with amino acids, amino sugars, peptides, and aliphatic compounds involved in linkages between the aromatic groups. The hypothetical structure for HA contains free and bound phenolic OH groups, quinone structures, nitrogen, and oxygen as bridge units and COOH groups variously placed on aromatic rings (Demirbas, 2002).

A variety of biomass types has been shown to have good biosorption potential and several have been proposed as the basis for treatment for metal-bearing industrial wastewaters (Gao et al., 1999; Lalvani et al., 2000; Perminova et al., 2005; Kyziol et al., 2006; Martyniuk and Wieckowska, 2003; Gode and Pehlivan, 2007; Alvarez-Puebla et al., 2006; Mor et al., 2007; Gode and Moral, 2008). Compared to techniques such as precipitation, ion exchange and reverse osmosis, biosorption process, metal sorption with HA offers the advantages of low cost and good efficiency. As a low cost, particulate brown coal is an attractive and inexpensive option for the biosorption removal of dissolved metals (Brown et al., 2000; Lakatos et al., 2001; Pehlivan and Arslan, 2006, 2007). HAs provide relatively cheap alternatives for Cr^{3+} ion removal compared to other some natural sorbents (Lakatos et al., 2002). HAs can be used to determine dissolved chromium in industrial wastewater effluents. Cr^{3+} may exist in the aqueous phase in different anionic forms, such as chromate (CrO_4^-), dichromate ($Cr_2O_7^{2-}$), or hydrogen chromate ($HCrO_4^-$), with total chromate concentrations and pH dictating which particular chromate species is predominant (Bayat, 2002; Dakiky et al., 2002).

Various metal-binding mechanisms are thought to be involved in the biosorption process including ion exchange, surface adsorption, chemisorption, complexation, and adsorption–complexation (Gode and Pehlivan, 2003; Arslan and Pehlivan, 2007). Brown coal is a complex material whose many constituents, especially lignins and HAs bear various polar functional groups including carboxylic and phenolic acid groups, which can be involved in metal binding. HAs obtained from brown coal are the mixture of polyelectrolytes covering a wide range of molecular weight and containing carboxyl and hydroxyl functional groups. Cr^{3+} is bound with the chelating activity of phenolic and carboxylic groups of humic acids and metal ion coordination activity (Kislenko and Oliynyk, 2004). Cr^{3+} ion with HAs is one of chelate ring formation involving adjacent aromatic carboxylate –COOH and phenolic –OH groups or, less commonly, two adjacent –COOH groups, which participate in ion-exchange reactions by binding metal ions with the release of H^+ ions. Cation biosorption is maximum at higher pH ranges, though different metals exhibit maximum binding at different pH values (Yu et al., 2003; Lakatos et al., 2002; Novak et al., 2001).

The Anatolian region of Turkey offers several sources of such brown coal, called lignite, particularly near Konya. HAs obtained from three towns in Konya, Ilgın, Beysehir and Ermenek, which have considerable reserves of lignite about 400.000 tonnes. The first two lignites seem to be, based on a lower calorific value, younger than the lignite from Ermenek. The present study has been aimed at the potential application of HAs as the sorbents for removal of Cr^{3+} ion from aquous solution. Experiments were performed in a certain range of contact time, solution pH, and initial metal concentration in solution, temperature and amount of adsorbent values. The operation of sorption for the removal of Cr^{3+} was carried out in batch vessels.

2. Methods

2.1. Chemicals

All solutions were prepared from analytical grade chemicals and Mili-Q filtered deionized water. 1.10^{-3} M of Cr^{3+} stock solution was prepared by dissolving 0.4002 g of $Cr(NO_3)_3 \cdot 9H_2O$ (from Merck). The working solutions with a concentration of 1.10^{-4}–1.10^{-3} M Cr^{3+} were prepared by appropriate dilutions of the stock solution immediately prior to their use. AC was purchased from Merck. The electrolyte used to modify the ionic strength in the adsorption experiments was 0.1 N $NaNO_3$.

2.2. Preparation of HAs from lignites

Three samples of lignite: Ilgın, Beysehir and Ermenek (middle part of Anatolia) were taken from the coalfield of the mines. All HAs were prepared from the three types of lignites. The characteristics of the lignites and HAs used in this study are summarized in Tables 1 and 2. The samples were ground to a particle size of 100 mesh using a ceramic mill. For this purpose, 1.0 g of the lignite sample was placed in 10 ml of distilled water and 30 ml of 5% NaOH was added to the suspension. The suspension was boiled for 3 min, then cooled and centrifuged at 3200 rpm. The supernatant was decanted and 30 ml of water was added to it. This suspension was again centrifuged, the superna-