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Comparing the efficacy of a novel waste-based adsorbent with PAC for the simultaneous removal of chromium (VI) and cyanide from electroplating wastewater

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ABSTRACT

The potential of powdered pistachio hull (PHP) for the co-adsorption of Cr(VI) and cyanide from electroplating wastewater was compared to that of powdered activated carbon (PAC). The results of dynamic adsorption experiments indicated that the complete and simultaneous removal of Cr(VI) and cyanide from wastewater was achieved with 2 g/L of PHP after 60 min of contact. Alternatively, with PAC, 69.2 and 77.8% of Cr(VI) and cyanide, respectively, were removed under the same conditions. Adsorption of Cr(VI) and cyanide by PHP and PAC followed pseudo-second order kinetics, and the equilibrium adsorption data best fit the Langmuir isotherm. The maximum capacity of PHP for the co-adsorption of Cr(VI) and cyanide was 117.6 and 151.5 mg/g, respectively, and the maximum capacity of PAC for the adsorption of Cr(VI) and cyanide was 47.6 and 39.4 mg/g, respectively. It was found that which intraparticle diffusion controlled the adsorption of Cr(VI) and cyanide onto PHP and PAC under the selected conditions. Overall, PHP efficiently adsorbed Cr(VI) and cyanide from industrial effluents; thus, PHP is an affordable and cost-effective system for the treatment of wastewater.

Keywords: Electroplating wastewater; Chromium; Cyanide; Adsorption; Agricultural waste

1. Introduction

The electroplating industry generates wastewater with high concentrations of cyanide ions and various heavy metals (Monser and Adhoum, 2002; Srisuwan and Thongchai, 2002); thus, the control of pollutants from the effluent of the electroplating industry is important for preserving human and environment health. Hexavalent chromium (Cr(VI)) and cyanide are among the most toxic compounds in electroplating baths and wastewater. Namely, exposure to Cr(VI) and/or cyanide causes adverse health effects in humans and other organisms (Dash et al., 2009; Rao and Rehman, 2010); therefore, these contaminants must be separated from electroplating industrial effluents before being discharged into the environment.

Several techniques have been investigated for the removal of Cr(VI) and cyanide as separate contaminants in aqueous and industrial wastewater. The most common method for the removal of Cr(VI) is the acidic reduction of Cr(VI) to Cr(III) and subsequently as chromium hydroxide (Módenes et al., 2010). Alternatively, alkaline chlorination/oxidation and chemical precipitation are conducted to remove cyanide from wastewater (Marder et al., 2004). Conventional methods of Cr(VI) and cyanide removal have several drawbacks including the generation of hazardous sludge, which is difficult to handle and discard, using chemicals to regulate the pH, to reduce Cr(VI) and oxidize cyanide, as well as to produce metal; thus, multiple reactors are needed to process the sludge. However, when Cr(IV) and cyanide are present in wastewater, the removal of Cr(VI) and cyanide with conventional techniques is more complex because the reduction of Cr(VI) to Cr(III) is conducted under acidic conditions ($pH \sim 3$), and the chlorination of cyanides requires alkaline media ($pH \approx 10$).

Due to the aforementioned limitations, conventional techniques are not attractive for the treatment of industrial effluents containing Cr(VI) and cyanide. Therefore, a novel and efficient treatment method for the simultaneous removal

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of Cr(VI) and cyanide from industrial effluents must be developed.

Adsorption onto a solid material is a practical method for the simultaneous removal of Cr(VI) and cyanide from contaminated streams. To reduce the costs of adsorption, researchers have investigated the adsorption potential of low-cost materials derived from agricultural wastes to identify an efficient and low-cost surrogate for activated carbon (Moussavi and Khosravi, 2011). For instance, the adsorption of Cr(VI) onto several agricultural waste materials has been investigated (Moussavi and Barikbin, 2010; Miretzky and Cirelli, 2010). Among the studied materials, powdered pistachio hull (PHP) displayed the highest Cr(VI) adsorption capacity (116.3 mg/g) (Moussavi and Barikbin, 2010). Thus far, the efficacy of rice husk (Yazıcı et al., 2009) and PHP (Moussavi and Khosravi, 2010) for the adsorption of cyanide from aqueous solution has been evaluated, and a maximum adsorption capacity of 0.401 and 156.2 mg/g was obtained, respectively. Therefore, further research must be conducted to understand the behavior of co-adsorption of Cr(VI) and cyanide in waste streams on the adsorption process onto waste materials.

In this study, the potential of a powder prepared from pistachio hull waste for the simultaneous uptake of Cr(VI) and cyanide from electroplating wastewater was compared to that of powdered activated carbon (PAC). The dynamics and equilibrium of the simultaneous adsorption of Cr(VI) and cyanide from electroplating wastewater was investigated at different concentrations of powdered pistachio hull (PHP) and PAC.

2. Materials and methods

2.1. Materials

The wastewater used in the present study was obtained from the electroplating bath of a local plant in Aliabad Industrial Park, Tehran, Iran. Chromic acid, sodium cyanide, and sodium hydroxide were added to the electroplating bath to plate metal parts. The wastewater was collected, transferred to the laboratory, characterized, and preserved in a refrigerator at 4 °C. The main characteristics of the wastewater were as follows: pH = 3.2, Cr(VI) = 85.5 mg/L, CN^- = 36 mg/L, and electrical conductivity = 5.65 ms/cm. Thus, the wastewater contained high concentrations of Cr(VI) and cyanide, which are toxic to organisms. The preserved wastewater was used as received in the adsorption experiments, and the procedures used to prepare the pistachio hull powder (PHP) and to determine the characteristics of the PHP have been described in the literature (Moussavi and Barikbin, 2010; Moussavi and Khosravi, 2010). In summary, PHP is a microporous adsorbent with a specific surface area of 1.04 m^2/g and a pH of zero point charge of 4.9. All other chemicals used in the present study were of analytical grade (Merck Co.). Powdered activated carbon (PAC) was prepared from commercial granular activated carbon (Merck Co.) with a specific surface area of 950 m^2/g.

2.2. Experimental methods

The adsorption experiments were conducted in 250-mL glass beakers equipped with a paddle-type mixer. The following experimental procedure was used to investigate the effect of the PHP concentration (1–5 g/L): 100 mL of wastewater was transferred into each beaker, and the desired amount of PHP was added to the flask. The mixer was turned on, and the suspension was stirred at 50 rpm for a preset duration (5–60 min). Upon completion, the suspension was filtered through a Whatman paper filter with a pore size of 0.45 μm, and the filtrate was analyzed for residual chromium (VI) and cyanide ions. Each test was conducted in duplicate to ensure that the results were reproducible, and the average results were reported.

Isotherms of the adsorption of Cr(VI) and cyanide from wastewater onto PHP were determined by conducting equilibrium adsorption experiments. The equilibrium adsorption experiments were carried out according to the same procedure used to investigate the effect of the PHP concentration; however, the mixing time was increased to 12 h to ensure that equilibrium was attained. All of the experiments were conducted at the natural pH of the wastewater (ca. 3.2). To determine the potential of PHP for the adsorption of the target ions, similar experiments were conducted with a commercially available (Merck Co.) powdered activated carbon (PAC).

2.3. Analytical methods

The concentration of cyanide in the raw and treated wastewater samples was determined by titration with a standardized solution of $AgNO_3$, as described in the Standards Methods (APHA et al., 1998). The Cr(VI) concentration was measured by reacting Cr(VI) with 1,5-diphenylcarbazide under acidic conditions and determining the absorbance of the solution with a spectrophotometer (Unico-UV 2100) at 540 nm (APHA et al., 1998). The pH and electric conductivity (EC) were measured with a Jenway Co. electrode and Hack 2100N EC meter, respectively.

2.4. Data analysis

The performance of PHP for the adsorption of Cr(VI) and cyanide from wastewater was evaluated by determining the removal efficiency (RE) and adsorption capacity (q_t, mg/g) of the material, according to the following equations:

$$\mathrm{RE} = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 and C_e are the initial and equilibrium concentration of each ion (mg/L), respectively. m is the mass of PHP added to the beaker.

To evaluate the kinetics of Cr(VI) and cyanide adsorption onto different concentrations of PHP, the experimental results were fitted to the pseudo-first and pseudo-second order reaction model, which have the following linear form under boundary conditions of $q = 0$ at $t = 0$ and $q_t = q_e$ at $t = t_e$:

$$\text{Pseudo-first order equation}: \quad ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

$$\text{Pseudo-second order equation}: \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

Intraparticle diffusion was evaluated using the equation developed by Weber and Morriss:

$$\text{Weber and Morriss equation}: \quad q_t = k_{id} t^{0.5} + C \tag{5}$$

where k_1 and k_2 are the adsorption rate constants, q_t is the adsorption capacity at time t, and q_e is the adsorption