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Synthesis of Al_2O_3/carbon composites from wastewater as superior adsorbents for Pb(II) and Cd(II) removal

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ABSTRACT

Al_2O_3/carbon (Al_2O_3/C) composites obtained from the alkaline wastewater of oil refinery and acid wastewater of aluminum anodizing factory have been studied with the principle of "using waste to treat waste". The process includes these steps: (1) acid-alkali neutralization, (2) evaporation, (3) calcination, (4) washing and drying. The Al_2O_3/C composites prepared by calcinating the precursors under Ar atmosphere are used as high-capacity adsorbents for removal of Pb(II) and Cd(II) from aqueous solutions. For Pb(II), the adsorptive behavior satisfies the Langmuir assumptions and the maximum adsorption capacity reaches to 709.2 mg g^{-1}. For Cd (II), the adsorptive behavior satisfies the Freundlich assumptions and the equilibrium adsorption capacity is up to 1299.4 mg g^{-1}. For single adsorption of Pb(II) and Cd(II), the adsorption kinetics follows Pseudo-second-order model well. This route shows a possible way of reducing emissions to the environment, recovering resource as a valuable material, and providing a novel strategy for wastewater treatment.

1. Introduction

Nowadays, with the rapid development of industry, more and more environmental pollution problems have been brought into focus. Although people get immense economic benefit from it, it also inevitably produces lots of pollutants in air, soil, especially in water. Water pollution has put agriculture, environment, and human survival into a dangerous situation [1–4]. Accordingly, water treatment plays an increasingly important role in human daily life. Meanwhile lots of methods have been developed and practiced for water treatment in recent a few decades, which includes filtration, screening, micro-filtration, centrifugation, evaporation, ion exchange, adsorption, photocatalysis, etc [5–7].

Alkaline wastewater is generated from petroleum refinery, which contains plenty of aliphatic and aromatic organic pollutants. These contaminants pose serious toxic hazards to environment. What's more, methods for treating those effluents such as coagulation [8], chemical oxidation [9], photocatalytic degradation [10], and biological techniques [11] have also been reported. Generally, these methods involve transfer of pollutants from one medium to another; therefore, another step is asked for the elimination of organic compounds, which makes total treatment process become more complex and expensive. Acid wastewater is another major pollutant in aluminum anodizing industry. Anodizing is an electrochemical process to form an oxide film over aluminum layer, which can provide hardness and corrosion resistance to aluminum products. This process will consume large amount of electrolytes (sulphuric acid, phosphoric acid, hydrochloric acid, etc. [12]) and generate large quantities of wastewater, which contains large amounts of aluminum ion (Al^{3+}) and hydrogen ion (H^+). At present, the most conventional and popular treatment of waste acid is neutralization by mixing them with excessive lime milk in area of Xinjiang, China. However, the whole process needs to cost large amount of lime milk and produces a great deal of waste residue which is hard to be recovered and recycled. Therefore, it's highly essential to adopt an effective way to control these wastewater.

"Using waste to treat waste" [13–16] is a new trend for pollutant control. In the present study, an innovative method is proposed to treat two kinds of wastewater according this principle. With a facile neutralization process, two types of wastewater are mixed and dried to produce a precursor containing Al^{3+}, organic matter and sodium sulfate (Na_2SO_4). Subsequently, the as-prepared precursors

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are calcinated under Ar atmosphere at high temperature to obtain Al_2O_3/C composites. During the calcination process, the abundant organic matters can serve as a carbon source, and Na_2SO_4 can be directly used as a sacrificial template according to the melting salt method [17–19].

Heavy metals are basically recognized to be a threat toward ecosystems and humans because of their high potential toxicity. Besides, they can not be biologically decomposed into harmless materials and, to matters worse, are accumulated in the organisms [20]. Until now, adsorption is one of the most effective technologies of advanced wastewater treatment which is employed to reduce hazardous organic/inorganic pollutants present in the effluent by industries [21]. What's more, synthesizing alumina-coated carbon materials as an adsorbent for heavy metal ions removal has already been researched by some groups [22]. Thus, in the present work, two heavy metal ions (Pb(II) and Cd(II)) are induced as the model pollutants to study adsorption performance of Al_2O_3/C composites. The work have been completed in the present research including: i) Determine the optimal calcinating temperature. ii) Characterize the adsorbents with XRD, SEM equipped with an EDX analyzer, BET, and Raman. iii) Examine Pb(II) and Cd(II) sorption isotherms and kinetics onto Al_2O_3/C composites. This versatile method exhibits a promising application in water treatment, and provide a recyclable strategy to control waste by waste.

2. Materials and methods

2.1. Materials

Alkaline and acid wastewater were obtained separately from oil refinery of Dushanzi Petrochemical Corporation (Xinjiang, China) and aluminum anodizing factory of Joinworld Co., Ltd. (Xinjiang, China). The analysis of wastewaters were illustrated in Table 1. Sodium hydroxide (NaOH) was purchased from Tianjin Baishi Chemical Co., Ltd and was of analytical grade. All aqueous solutions were prepared with deionized water.

2.2. Preparation of Al_2O_3/C composites

In a typical synthesis, 150 mL of alkaline wastewater was filtered into a conical flask, and 200 mL of acid wastewater was added into conical flask. Then, 0.01 mol L^{-1} of NaOH solution was added to the mixture drop by drop with shaking to adjust pH value to 9. At the same time, the mixture appeared a precipitation, and the precipitation did not dissolve within 5 s. The obtained mixture was transferred to a watch glass, and dried at 80 °C in air. After drying, mixture was grounded in a mortar to form a fine powder. Subsequently, the powder was calcinated at a target temperature (550, 600, and 650 °C: noted as S-550, S-600, and S-650) with a heating rate of 10 $°C\cdot min^{-1}$ and kept at that temperature for 3 h under argon atmosphere. After cooling down, the products were washed with deionized water and dehydrated in a vacuum freeze dryer. Finally, the Al_2O_3/C composites were prepared by this method.

2.3. Characterizations

The morphology and chemical compositions of samples were characterized by a field-emission scanning electron microscopy (FESEM) in a Hitachi SU8010 equipped with a link energy-dispersive spectroscopy (EDS) analytical microprobe. The crystal structure of the samples were determined by X-ray diffraction (XRD, BRUKER D8 with Cu Kα radiation (λ = 1.54178 Å)). The Brunauer-Emmett-Teller (BET) specific surface area and pore volume were measured on a nitrogen adsorption apparatus (JW-BK, China) at 77 K. Desorption isotherms were used to calculate the pore size distributions using the Barret-Joyner-Halender method. Raman spectra were measured by Bluker Senterra with 532 nm wavelength laser source.

2.4. Batch adsorption test

To investigate removal of samples (S-550, S-600, S-650) prepared with different temperatures, a series of adsorption experiments were conducted using lead nitrate ($Pb(NO)_2$) and Cadmium nitrate (Cd $(NO)_2$) as a simulation of pollutants in water. 30 mg of Al_2O_3/C composites were well-dispersed into 50 mL of Pb(II) and Cd(II) solutions (100 mg/L) separately with a constant stirring in the dark. Then, samples were drawn from solution at predetermined time intervals, and centrifuged to measure the Pb(II)/Cd(II) removal via an atomic absorption spectroscopy (Hitachi, Z-2000, Japan). The metal ions removal efficiency R (%) were calculated by Equation (1):

$$R = [(C_0 - C_t)/C_0\ ]^*\ 100 \quad (1)$$

here C_0 (mg L^{-1}) is the initial metal ion concentration and C_t (mg L^{-1}) is residual metal ion concentration in solution at any time t (min).

To estimate adsorption capacity, 50 mg of S-600 was added to 100 mL of Pb(II) and Cd(II) solutions respectively. These solutions, with different concentrations (100–1000 mg L^{-1}), were stirred in the dark at equilibrium time. Then the amounts of metal ion adsorbed on Al_2O_3/C composites, q_t (mg g^{-1}) were calculated by the following Equation (2):

$$q_t = (C_0 - C_t)\ V/m \quad (2)$$

here q_t (mg g^{-1}) was the adsorption capacity at any time t (min). V (L) was the volume of the solution, and m (g) is the mass of adsorbents.

3. Results and discussion

3.1. Characterizations of Al_2O_3/C composites

The XRD patterns of samples were showed in Fig. 1. In figure, samples exhibited complex crystal phase and peak position, because of complex composition of the two different wastewater. Also, some impure peaks appeared, and the major peaks could be identified as γ- Al_2O_3 and carbon [23], respectively, in Fig. 1. In order to figure out the element component of samples, the energy dispersive spectrometer (EDS) exhibited in Fig. 2(e–f) confirmed that the as-prepared products were mainly composed of C, O, and Al elements. Thus, it could be concluded from XRD and EDS images that Al_2O_3/C composites had been successfully synthesized. SEM images of as-prepared products were showed in Fig. 2(a–c). From Fig. 2(a–c), it could be seen that the morphologies of as-prepared products were different. S-600 was some porous thin sheets, while S-550 and S-650 were small nanoparticles. Combining SEM

Table 1
Chemical composition of alkaline wastewater and acid wastewater.

Alkaline wastewater	Contents (mg L^{-1})	Acid wastewater	Contents (mg L^{-1})
pH	13.4	pH	0.3
COD	50000–60000	Al	6329
Phenols	600	SO_4^{2-}	13269
Ammonia	3557	Fe	31
Sulphides	7500	Mg	52
TDS	20000	Ca	511