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Enhanced sorption of cadmium ion on highly ordered nanoporous carbon by using different surfactant modification

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ABSTRACT

This paper reported, the effect of different type of surfactants on the adsorption of Cd(II) on ordered mesoporous carbon was investigated using cationic, anionic and non-ionic surfactant. The structural order and textural properties of the mesoporous adsorbents was studied by XRD and nitrogen adsorption. Adsorption experiments were conducted in batch mode with the variables such as amount of agitation speed, contact time, temperature, initial solution concentration and solution pH. The Cd(II) removal for cationic surfactant cetylpyridinium chloride (CPC), non-ionic surfactant Triton X-100 (TX), anionic surfactant sodium dodecyl sulfate (SDS) modified mesoporous carbon and unmodified mesoporous carbons were found to be 94.5%, 88.4%, 84% and 68%, respectively. The sorption data were correlated better with the Langmuir adsorption isotherm than Freundlich isotherm.

1. Introduction

Heavy metals are toxic to aquatic flora and fauna even in relatively low concentrations. Some metals can be assimilated, stored and concentrated by organisms [1,2]. Industries, including mining and electroplating, discharge aqueous effluents containing high levels of such heavy metals as uranium, cadmium, mercury, and copper. Untreated effluents may have an adverse impact on the environment [3,4]. Heavy metals including cadmium, lead, and zinc, are toxic at high concentrations and are priority pollutants observed in municipalities and specific industries throughout the United States [5,6].

Cadmium is very toxic and causes serious damage to the kidneys and bones. It is best known for its association with itai–itai disease [7]. Cadmium ions have little tendency to hydrolyze at pH values <8 but above 11, all cadmium exists as its hydroxo-complex [8]. Cd(II) predominates in fresh water at pH 6–8. $Cd(OH)^+$, $Cd(OH)_2$, $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$ also exist depending upon the solution pH [1,7]. The chlorocomplexes $CdCl^+$, $CdCl_2$, $CdCl_3^-$ predominate in sea water and Cd(II) is present in very small amounts [7]. Cadmium accumulates in humans, causing erythrocyte destruction, nausea, salivation, diarrhea, and muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformity [2]. The major sources of cadmium release are the manufacturing of alloys, batteries, pigments and plastics. Mining and refining processes are also significant sources [9,10]. The drinking water guideline recommended by the WHO and AWWA is 0.005 mg Cd/L. In many ground waters that contain bicarbonate/carbonate anions the aqueous speciation of cadmium includes several complexes with bicarbonate/carbonate. Cadmium carbonate can be a solubility control for some elevated alkaline environments that contain high cadmium contamination.

A number of treatment methods for the removal of metal ions from aqueous solutions have been reported, mainly ion exchange, electrochemical reduction, evaporation, solvent extraction, reverse osmosis, chemical precipitation, membrane filtration and adsorption [5]. Most of these methods involve high capital cost and are not suitable for small-scale industries. The adsorption processes are generally known to be one of the most effective techniques for removal of environmentally hazardous metals. As it is easy to remove the adsorbent from aqueous media after treatment, adsorption technique is generally considered to be a promising method and has been studied for chromate removal as well. Adsorbents with strong affinity and high loading capacity for targeted metal ions have been developed by modifications of the surface of various substrates, such as polymers and clays with metal complexing groups [6,7].

The most common adsorbent material is activated carbon-based adsorbents, which has a huge specific surface area, plentiful micro and macro pores, and a high adsorption capacity. These adsorbents is economically favorable because it can be made from

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various low-cost materials that have high carbonaceous content including wood, coal, petroleum coke, sawdust and coconut shell [8]. However, applications of activated carbon-based adsorbents, with large fraction of micropores (<2 nm) occupying most pore volume, can be limited by slow diffusion kinetics for some applications [9,10]. Recently, Ryoo et al. prepared ordered mesoporous carbons (CMK-x) from mesoporous silica templates such as MCM-48, SBA-1 and SBA-15 using sucrose as the carbon source [11–14]. Mesoporous carbon materials with ordered pore structure, high pore volume, high specific surface area, and tunable pore diameters can be prepared using the hard template method [12]. Due to its open pore structure and mesoporous properties, mesoporous carbon provides marked advantages over typical activated carbon in the adsorption and diffusion process. Marked achievements in the study of mesoporous materials have been made in material preparation and catalysis application. Recently, a surface modification technique has been reported to enhance the adsorption rate and capacity of carbon-based adsorbents [8,15]. A surfactant is an amphipathic structure along with a hydrophobic group and together a hydrophilic group. Surfactants are adsorbed onto solid surface and change the surface properties of solids, especially at the interface. In recent years, the use of surfactants in water and wastewater treatment has been specially preferred to separation of metal ions and other toxic substances [16–18].

In this study, the effect of surfactants on the adsorption of Cd(II) onto highly ordered mesoporous carbon was investigated using a cationic, anionic and non-ionic surfactant. The influence of the surfactants was analyzed in terms of adsorption rate (adsorption kinetic) and capacity (adsorption isotherm) for Cd(II). The pH effect was evaluated doing tests at different pH solution conditions. Interestingly, it has been found that the adsorption capability of different types of surfactant modified ordered mesoporous carbon for cadmium ion is much higher compared to that of pristine mesoporous carbon. Furthermore, Langmuir and Freundlich adsorption isotherms were studied to explain the sorption mechanism.

2. Method

2.1. Materials

The reactants used in this study were tetraethyl orthosilicate (TEOS) as a silica source, cetyltrimethylammonium bromide (CTAB) as a surfactant, sodium hydroxide (NaOH), sodium fluoride (NaF), and deionized water for synthesis of mesoporous silica (MCM-48) and sucrose as a carbon source, and sulfuric acid as a catalyst for synthesis of mesoporous carbon, The surfactants used were the cationic surfactant cetylpyridinium chloride (CPyCl), anionic surfactant sodium dodecyl sulfate (SDS), $CH_3(CH_2)_{11}SO_4^-Na^+$, non-ionic surfactant Triton X-100 (TX-100, $C_8H_{17}C_6H_4O(CH_2CH_2O)_{9.5}H$). The all chemicals were analytical grade and were purchased from Merck (Darmstadt, Germany).

Standard stock solution (1000 mg/L), of Cd(II), was purchased from Merck (Darmstadt, Germany); working standard solutions were prepared by appropriate dilution of the stock standard solution. The following buffers were used to control the pH of water samples: hydrochloric acid–glycine (pH 1–3), sodium acetate–acetic acid (pH 3–6), disodium hydrogen phosphate–sodium dihydrogen phosphate (pH 6–8), and ammonium chloride–ammonia (pH 8–10).

2.2. Synthesis of silica template and OMC

High-quality MCM-48 sample was prepared following the synthesis procedure reported by Baek and Yang [19]. Then 1.25 g sucrose and 0.14 g H_2SO_4 in 5.0 g H_2O was dissolved, and this solution were added to 1 g MCM-48. The sucrose solution corresponded approximately to the maximum amount of sucrose and sulfuric acid that could be contained in the pores of 1 g MCM-48. The resultant mixture was dried in an oven at 373 K, and subsequently, the oven temperature was increased to 433 K. After 6 h at 433 K, the MCM-48 silica containing the partially carbonizing organic masses was added with an aqueous solution consisting of 0.75 g sucrose, 0.08 g H_2SO_4 and 5.0 g H_2O. The resultant mixture was dried again at 373 K, and subsequently the oven temperature was increased to 433 K. The color of the sample turned very dark brown or nearly black. This powder sample was heated to 1173 K under vacuum using a fused quartz reactor equipped with a fritted disk. The carbon–silica composite thus obtained was washed with 1 M NaOH solution of 50% ethanol–50% H_2O twice at 363 K, in order to dissolve the silica template completely. The carbon samples obtained after the silica removal were filtered, washed with ethanol and dried at 393 K.

2.3. Chemical modification of OMC

Chemical modification of prepared ordered mesoporous carbon was done by immersing 5 g of adsorbent in 100 mL, micellar solution of cationic, anionic and non-ionic surfactants for 4 h. Adsorbents were separated using Whattman filter paper, rinsed with deionized water, dried in an oven overnight at 383 K, sieved to the required sizes and stored in desiccators for further applications.

2.4. Characterization

The X-ray powder diffraction patterns were recorded on a Philips 1830 diffractometer using Cu Kα radiation. The diffractograms were recorded in the 2θ range of 0.8°–10° with a 2θ step size of 0.01° and a step time of 1 s. Adsorption–desorption isotherms of the synthesized samples were measured at 77 K on micromeritics model ASAP 2010 sorptometer to determine an average pore diameter. Pore-size distributions were calculated by the Barrett–Joyner–Halenda (BJH) method, while surface area of the sample was measured by Bruner–Emmet–Teller (BET) method.

2.5. Adsorption studies

Adsorbate stock solution (1000 mg/L) was prepared by dissolving Cd(II) salt in 1% HNO_3 solution to prevent hydrolysis formation. Salt used was $Cd(NO_3)_2$, with high degree of purity. The stock solution of Cd(II) was diluted with distilled water to obtain standard solutions. Batch adsorption isotherms were performed by shaking 0.5 L amber Winchester bottles containing the required concentration of the Cd(II) in a Gallenkamp incubator shaker. The shaker was set at a temperature of 25 ± 1 °C and a speed of 150 rpm. Initial solution concentration of 0.12–1.20 mmol/L was prepared by pipetting out the required amounts of the Cd(II) from the stock solution. The volume of solution in each bottle was maintained at 0.5 L and the solutions were adjusted to pH 7. About 0.01 mg of each adsorbent was weighed accurately on aluminum foils using a Sartorious (Model BP 201D) analytical balance. The adsorbents were transferred carefully into the bottles using 50 mL solutions from the bottles. The bottles were shaken vigorously before shaking for different time in the incubator shaker (New Brunswick Scientific C25 Model). An atomic absorption spectrometer, Shimadzu AA-6300 (Kyoto, Japan) with a deuterium background correction, equipped with a graphite furnace atomizer (GFA-EX7i), was used for this work. The cadmium hollow cathode lamp (Hamamatsu Photonics, Shizuoka, Japan) was run under the conditions recommended by the manufacturer (current: 10 mA). Also, the wavelength (228.8 nm), the slit bandwidth (0.7 nm) had conventional values. High-density graphite-coated tubes (Shimadzu) were used.