



Kinetics of copper ions sorption onto activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles

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ABSTRACT

The paper deals with comparative kinetics studies of copper ion sorption onto three different carbon sorbents: activated carbon, carbon nanotubes and carbon-encapsulated magnetic nanoparticles. The studied sorbents possess many structural and morphological differences, which include the primary particle size, grain size, graphitization degree, surface area and density of surface acidic groups. The kinetics studies were performed at base and acidic pHs and involved various starting concentrations. It has been found that nanostructured carbon sorbents adsorb the Cu(II) ions faster than activated carbon. The density of surface functional groups was found to be a parameter that primarily drives the sorption rates.

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1. Introduction

Heavy metal ions are dangerous constituents of wastewaters because of their toxicity to living systems even at low concentrations [1]. Thus, removing of heavy metal ions from sewages, before their release to the environment, is a key problem of modern wastewater treatment. By far various porous materials were used for removal of metals from aqueous solutions, e.g. activated carbon (AC) [2–4], ion exchange resins and polymers [5,6], chitosan [7], porous ceramic supports with immobilized ion chelating agents [8]. An increased attention is being observed for various nanomaterials, e.g. carbon nanotubes (CNTs) [9–11] and functionalised nanoparticles [12]. These nanomaterials seem to be attractive for prospective environmental applications, because their sorption characteristics are better in comparison to conventional adsorptive materials.

Recently, an increased attention has been paid to composite materials that combine sorption properties and intrinsic mobility. It is especially seen in composites of activated carbon and magnetic nanoparticles [13], in which the presence of magnetic phase facilitates the recovery of the sorbent from the cleaned solution. These composites can be easily moved by using simple and low-cost permanent magnets. Nevertheless, such magnetic sorbents have a major drawback, i.e. the magnetic nanoparticles are located within the pores and this does not protect them from contact with

the solution. It is important for acidic environments, in which the magnetic phase can be leached out. Carbon-encapsulated magnetic nanoparticles (CEMNPs) are free of this disadvantage, because they consist of uniform spherical nanocrystallites tightly covered by tight carbon coatings. The coatings not only protect the encapsulated nanoparticles from agglomeration and corrosion. Their role is to provide a scaffold for introducing surface acidic groups that are essential to bind the metal ions [14–16].

The sorption capacity is one of the most important parameter of the sorbent characteristics because it determines how much of the pollutant can be removed from the cleaned solution by a unit mass of the sorbent. Nevertheless, high values of sorption capacities are not sufficient in broad application areas. The adsorption kinetics is the second feature that may also strongly constrain the applicability of the sorbent. The low sorption kinetics significantly enlarges the operation time, what makes the removal processes unfavourable.

The aim of this work includes comparative kinetic studies of Cu(II) ion adsorption onto three carbon-based sorbents: activated carbon, carbon-nanotubes and carbon-encapsulated magnetic nanoparticles. It has been showed in our recent work, that these materials have substantially distinct sorption efficiencies, which are influenced by various morphological and structural features, e.g. morphology, primary particle size, crystallinity, surface area and density of active binding sites [16]. It has been found, that most of these parameters affect the sorption efficiencies [16]. In the present paper we investigate whether such large morphological, structural and textural differences may also influence the sorption kinetics.

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2. Experimental

2.1. Materials

Activated carbon in a form of granules (20–60 mesh and multi-wall carbon nanotubes (50–100 nm in diameter, purity above 95%) were obtained from Sigma–Aldrich. Carbon-encapsulated magnetic nanoparticles were produced by a carbon arc plasma route [17]. In brief, the arc was ignited between graphite cathode and graphite anode doped with iron powder. The high temperature within the carbon arc allowed iron and carbon to evaporate. Then the Fe–C vapour rapidly condensed to form carbon-encapsulated iron nanoparticles. The as-obtained raw products were refluxed in boiling 4 M HCl for 24 h with further cleaning in excess of water and ethanol and drying in air. This purification procedure resulted in removing the by-products, which were mainly composed of iron particles that have not been encapsulated in protective carbon shells.

Prior to use, in order to create binding sites on the sorbent surface, 2 g of carbon materials were soaked in 50 mL of 8 M HNO₃ for 12 h (25 °C). Then the suspensions were filtered through a 0.45 μm membrane filter and the sorbents were washed with deionized water until a neutral pH was obtained. The treated carbon-based sorbents were dried at 90 °C for 2 h and stored for further use.

2.2. Adsorption kinetic studies

Analytical reagent-grade chemicals were used as well as deionized water from a Milli-Q system (Millipore). The Cu(II) solutions were prepared from a 1000 mg/L stock solution of copper nitrate (Merck). The concentration of metals was determined by atomic absorption spectrometry using a Perkin Elmer 3110 apparatus. The instrumental settings of the manufacturer were followed. For kinetic studies 50 mg of the appropriate sorbent was added to the flask containing 10 mL of Cu(II) solution (concentration range 2–20 mg/L) at pH 8.0. Tests at pH 5.0 were additionally conducted on Cu(II) solution with concentration of 10 mg/L. The obtained mixture was gently shaken for 4 h at room temperature (20 ± 1 °C). Specific amounts of solution were withdrawn at various time intervals and analysed to estimate the copper ion uptake.

3. Results and discussion

3.1. Morphological and structural characterization of sorbents

The morphological and structural characteristics of the studied sorbents are described elsewhere [16]. Here, we presented the data which directly correspond to the adsorption kinetics and will be useful for interpretation of the results. Fig. 1 shows representative optical and SEM images. The carbon sorbents have completely distinct morphological features. Carbon encapsulates consist of primary particles that have diameters below 100 nm. Similarly, carbon nanotubes comprise the individual tubular objects 50–100 nm in diameter and length up to several microns. Activated carbon is built of large grains that have well defined porous structure. Both of these nanostructured sorbents in a contact with polar solvents (e.g. aquatic solutions of heavy metal salts) form agglomerates significantly exceeding the sizes of their primary particles. This is a consequence of the surface hydrophobic character. The mean diameter of these agglomerates were estimated assuming their elliptical shape (the mean diameter was taken as the average of the major and minor axis of the ellipse). The mean diameter was obtained from analysing at least 100 objects on optical microscope images (Table 1). The diameters of the nanostructured sorbent agglomerates are lower in comparison to the activated carbon, however all of them are in the same range. Importantly, the estimated diame-

ters of the AC are in satisfactory agreement with the data provided by the manufacturer (20–60 mesh = 250–841 μm). This shows that the applied method (optical microscopy imaging) gives reasonable results. The sorbents also differ with the crystallinity of the carbon phase (usually named as graphitization), which can be expressed as the G/D ratio. This parameter is a ratio between the two bands (the so-called G and D bands), which appear on the Raman spectrum of the solid carbon materials. The G band originates from the stretching vibrations within the basal graphene layers that form the solid particles of the studied carbon material. The D band is associated with the structural disorder and its intensity rises when the sample has poor graphitization, for example in the presence of defects (sp³ carbons, heptagons, dangling bonds, foreign atoms) and finite size effects [18]. The G/D ratios for the studied carbon sorbents (Table 1) point to significant differences in their crystallinity. The values for CEMNPs and CNTs are typical for materials built from graphitised layers with sufficient number of defects that are needed to introduce the curvature and close the carbon coatings covering the encapsulated nanoparticles. The G/D ratio for the activated carbon is ca. 3 times smaller in comparison to the values for CEMNPs and CNTs. It shows, that activated carbon has poor graphitization, and structural ordering in this materials reaches a few nm only.

Sorption of heavy metal ions is enabled when the surface of the sorbent is negatively charged and then it is capable for electrostatic binding the metal cation. The carboxylic groups were introduced onto carbon sorbents after controlled oxidation by HNO₃. The amounts of these groups referred to the unit mass are presented in Table 1. It is seen that each of the studied carbon materials has similar surface acidity, despite significant morphological and structural differences. Nevertheless, the sorbents differ with the distribution of acidic groups, which can be globally expressed as the surface charge density (SCD) [16]. The SCD can be calculated using a formula: $SCD = (SAC \times F/SA) (C m^{-2})$, where SAC is surface acidity (in mmol/g), SA is surface area (in m²/g) and F is Faraday constant (96.5 C/mmol). It is worth to highlight, that the amounts of the acidic groups and SCDs are reversibly depended on the mean diameter of agglomerates. Higher numbers of polar carboxylic groups in CEMNP sample decreases the hydrophobicity and allow for partial wetting of primary particles, what finally results in lower sizes of agglomerates.

3.2. Sorption kinetics

Fig. 2a–c show the effect of contact time on the sorption efficiency of Cu(II) ions at slightly base conditions (pH 8, initial concentrations of Cu(II) between 2 and 20 mg/L). At this pH all carboxylic groups introduced onto carbon sorbents during nitric acid oxidation are completely negatively charged and they are capable to bind Cu(II) cations. The ion uptake for the nanosized carbon sorbents reaches 90–95%, whilst the activated carbon is able to adsorb only 55% of initial amounts of Cu(II) in the respected time. Importantly, no significant differences were observed for distinct initial concentrations of metal ion, that broadly ranged between 2 and 20 mg/L. Another important finding shows that the AC sorbent does not reach the adsorption equilibrium even after 4 h. Such contact time is sufficient to yield the equilibrium for carbon encapsulates and carbon nanotubes. The half saturation times for nanostructured sorbents are less than 10 min. This qualitatively suggests that CNTs and CEMNPs adsorb the heavy metal ions much faster in comparison with typical activated carbons.

Adsorption kinetics of Cu(II) at acidic conditions (pH 5) is very distinct when compared to the base pH (Fig. 2d). Similarly to the base pH, there were no differences in adsorption kinetics for different initial concentrations. Therefore, the results for the concentration of 10 mg/L are presented only. First of all, the AC and CNTs sorbents have very weak affinity towards Cu(II) ions and the

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