Functionalization of polyacrylonitrile/Na-Y-zeolite composite with amidoxime groups for the sorption of Cu(II), Cd(II) and Pb(II) metal ions

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GRAPHICAL ABSTRACT
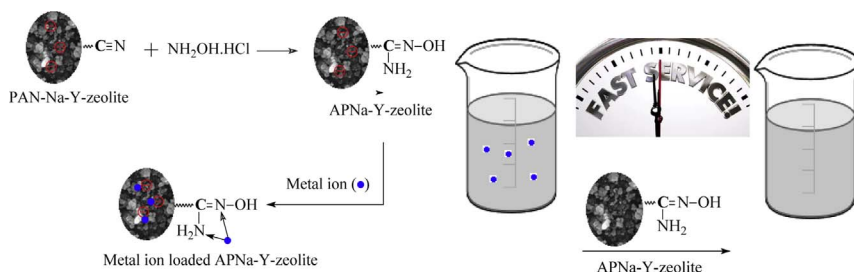
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ABSTRACT

A composite material (PAN-Na-Y-zeolite) was prepared by polymerization of acrylonitrile in the presence of Na-Y zeolite. The composite was functionalized by amidoximation through the reaction of hydroxylamine on nitrile groups of the composite. The sorbent (APNa-Y-zeolite) was fully characterized by FTIR spectrometry, XRD diffraction, thermogravimetric analysis, scanning electron microscopy, zetametry and BET analysis. The sorption properties of APNa-Y-zeolite were investigated for the recovery of Cu(II), Cd(II) and Pb(II) from synthetic solutions before being tested for the purification of local tap water. Sorption properties were characterized through the study of pH effect, uptake kinetics, sorption isotherms. The pseudo-second order rate equation fitted well kinetic profiles. Sorption isotherms were modeled using the Langmuir, the Freundlich and the Sips equations. Thermodynamic parameters were evaluated through variation of temperature. While the sorption of Cu(II) and Cd(II) was endothermic, Pb(II) recovery was exothermic. Metal ions were successfully desorbed using 5 M HCl solutions. High concentrations of NaCl hardly alter sorption performance, contrary to humic acid that slightly reduces metal binding.

1. Introduction

The contamination of water bodies by heavy metal discharge into the environment became a challenging issue for industry for the last decades. The international regulations on drinking water standard and the limit concentrations for discharge into the environment are becoming stricter [1]. The persistence and toxicity of these metals and their bioaccumulation at the different steps of the food chain may explain that the regulation laws are requiring very low metal standards [2,3]. Metals like copper, cadmium and lead are presentative of these hazardous metals that are strongly controlled in terms of health and environmental impact [4]. They are abundantly used in industry,

including mining, metallurgy [5,6], electroplating [7,8], textile, ceramics, batteries [9–11], etc.

Numerous processes have been designed for the removal of heavy metal ions from wastewaters. The application of these processes depends on the objective, including environmental objective for decreasing the concentration of hazardous contaminants, and the recovery of valuable metals that require high concentration effect and selective separation. Precipitation process allows easy removal of metal ions but produces huge amounts of contaminated sludge. The technique is generally poorly selective [12]; although some specific processes may contribute to separate target metals [8]. Solvent extraction [13,14] is a very efficient method for recovering metal ions in effluents containing relatively high metal concentrations (usually higher than several hundred of mg L^{-1}); however, the loss of toxic and expensive extractant by dissolving in water and physical dispersion limits the application to valuable metals and high concentration effluents. This technique is thus poorly competitive for low metal concentration (below 50–100 mg L^{-1}). For dilute solutions, sorption processes are generally more interesting, using, for example: ion-exchange and chelating resin [11], extractant impregnated resin [15–17], inorganic sorbents [18–20], activated carbon [21,22], carbon-based/polymer composites [23], biosorbents [24–28]. Zeolite materials are three-dimensional alumino-silicate frameworks constituted of tetrahedral SiO_4 and AlO_4 arrangements. they have a global anionic surface, which, in turn, is neutralized by an external cationic framework (constituted of Na^+, Ca^{2+} or Mg^{2+}). This opens the way to the binding of heavy metal cations by ion-exchange on natural zeolites [29]. Zeolite Y is an emblematic example of material having good textural properties [30], and sufficient availability for developing large-scale applications. However, the sorption properties are generally relatively weak and it is necessary functionalizing their surface for improving metal recovery.

Polymers offer many advantages for the elaboration of sorbents including the possibility to manage (a) the form and porosity of the sorbents, (b) the readily functionalization of the surfaces by grafting new reactive groups having higher affinity or selectivity for target metals. However, it may be interesting combining the advantages of these synthetic polymers with the high specific surface area of zeolite and other mesoporous materials: the deposition of the polymer at the surface of the porous support (through on-surface polymerization) may improve mechanical properties, textural characteristics, and then mass transfer performance of composite materials, which can be used for metal binding [31,32]. The polymerization of poly(acrylonitrile) at the surface of Na-Y-zeolite allows synthesizing composite supports that can be further functionalized by reaction with an alkaline solution of hydroxylamine hydrochloride to convert nitrile groups into amidoxime groups [33–35]. Amidoxime-based sorbents have been abundantly studied for the recovery of uranium from aqueous solutions [33,36–39], including sea water [40–46]. However, though less documented, amidoxime-based sorbents have also been investigated for heavy metal recovery [39,47–52].

This study describes the synthesis of a sorbent based on amidoxime functionalized PAN/Na-Y-zeolite. The material is characterized by scanning electron microscopy (SEM), X-ray diffraction, Brunauer-Emmett-Teller (BET) analysis, thermogravimetric analysis, FTIR spectroscopy and zetametry. In a second step, the sorption properties of the sorbent are evaluated through the study of pH effect, uptake kinetics, sorption isotherms. The thermodynamic parameters are also evaluated. Metal desorption and sorbent recycling are also tested. The sorption properties are evaluated in the presence of NaCl and humic acid, before testing the sorption properties in metal-spiked tap water.

2. Materials and methods

2.1. Materials

Acrylonitrile (AN) was supplied by Fluka AG (Buchs, Switzerland). Na-Y-zeolite, hydroxylamine hydrochloride, methanol, potassium persulfate were purchased from Loba Feinchemie GmbH (Fischamend,

Austria). Humic acid was obtained from Sigma-Aldrich Chemie GmbH (Munich, Germany). All reagents were analytical grade. Cu(II), Pb(II) and Cd(II) standard solutions (1000 mg L^{-1}) were used as stock solutions for preparing metal ion solutions; working solution were prepared by dilution just prior experimental tests. Tap water was collected on the municipal water network managed by Damietta Water Company (Damietta, Egypt).

2.2. Copolymerization procedure for PAN/Na-Y-zeolite synthesis

For the synthesis of the composite the precursors (acrylonitrile monomer and Na-Y-zeolite) were mixed with 50 mL of demineralized water: the AN/zeolite mass ratio was varied according the values 1:1, 1:2 and 1:3 (i.e.: 20 g of AN and 20 g, 40 g or 60 g of Na-Y-zeolite). A fixed amount (i.e., 0.1 g of potassium persulfate) was added as the initiator of polymerization reaction. The reaction was performed in a reactor equipped with a mechanical stirrer with a temperature controlled to 70 °C. After 4 h of reaction the solid (PAN-Na-Y-zeolite composite) was recovered by filtration, washed up with ethanol and air-dried. Actually, the experimental conditions were selected on the basis of the optimization of PAN polymerization by El-Sonbati et al. [53–55]; in addition, the proportion of mineral compound was experimentally optimized in the present study.

2.3. Functionalization of composite with amidoxime groups

The functionalization of the composite was performed by reaction of nitrile groups on PAN-Na-Y-zeolite using hydroxylamine [56]. First, hydroxylamine hydrochloride (42.1 g) was dissolved in 300 mL a methanol/water mixture (5:1, volume ratio); the solution was neutralized with NaOH to pH 10. The methanol/water ratio was controlled as close as possible to 5:1. Sodium chloride precipitate was removed by filtration. In a second step, the PAN-Na-Y-zeolite composite was dropped into the hydroxylamine solution. The reactor was equipped with a condenser and a mechanical stirrer. After 2 h of reaction at 70 °C, the sorbent was removed by filtration, washed up several times with methanol/water solution (4:1, volume ratio), before being treated with 200 mL of a 0.1 M HCl/methanol solution for 15 min. Finally, the sorbent was rinsed several times with a methanol/water solution (4:1, volume ratio) and dried at 50 °C (till constant weight). Scheme S1 shows the reaction pathway and the suggested structure of the sorbent (see Supplementary Material).

2.4. Characterization of the sorbent

The morphology of sorbent particles was characterized using a scanning electron microscope (JEOL-JSM-6510 LV, Jeol, Tokyo, Japan). The textural properties of the sorbent (BET surface, pore volume and pore size) were characterized using a Quantachrome NOVA 3200e surface area and pore analyzer; data analysis was performed using NovaWin software (v11.0) (Quantachrome Instruments, Boynton Beach, FL, USA). X-ray diffraction analysis was performed using a Shimadzu XRD-6000 diffractometer (Shimadzu Corporation, Tokyo, Japan) in the range 2θ: 5–80°, with Cu K$_\alpha$ radiation (λ = 1.540598 Å). Thermogravimetric analysis was operated on Shimadzu TGA-50 thermogravimetric analyzer (Shimadzu Corporation, Tokyo, Japan): analysis was performed under N$_2$ atmosphere with a temperature ramp of 10 °C min^{-1}, in the range 20–999 °C. FTIR analysis was carried out using a JASCO-FT/IR-4100 spectrometer (Jasco, Easton, MD, USA): the finely grinded samples were incorporated into KBr discs prior to analysis in the wavenumber range 400–4000 cm^{-1}. The zeta potential of the sorbent was measured using a Nano Zeta Sizer (Nano-ZS Malvern Instruments Ltd., London, United Kingdom) at various pHs from 1 to 8. A 0.01 g of the sorbent was mixed with 50 mL of 0.1 M KCl. The suspension was then adjusted to the specified pH and kept under stirring