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Research paper

Removal of Cs^+ and Co^{2+} ions from aqueous solutions using poly (acrylamide-acrylic acid)/kaolin composite prepared by gamma radiation

M.I. El-Dessouky[a], H.H. Ibrahiem[a], E.H. EL-Masry[a,*], G.E. Sharaf El-deen[a], N.M. Sami[a], M.E. Moustafa[b], E.M. Mabrouk[b]

[a] *Hot Labs, Atomic Energy Authority Inshas, Kaliobia, Egypt*
[b] *Banha University, Faculty of Science, Chemistry Department, Egypt*

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ABSTRACT

Synthesis of poly (acrylamide-acrylic acid)/kaolin composite (P(AM-AA)/K) using gamma radiation was carried out for removal of cesium and cobalt ions from aqueous solution. The prepared composite was characterized using FT-IR, SEM, XRD, TGA and DTA. Comparative adsorption behavior of poly (acrylamide-acrylic acid)/kaolin composite for adsorption of cesium and cobalt ions was studied. The adsorption studies were performed under different pH, temperature, and initial metal ion concentration. The obtained data are handled using adsorption kinetics, isotherm models and the thermodynamic behavior of the metal ion adsorption was calculated. It was found that the synthesized composite possesses a good swelling behavior due to the presence of kaolin. Pseudo-second-order kinetic model provided a better correlation for the experimental data in comparison to the pseudo-first-order kinetic model. The negative value of ΔG indicates the feasibility and spontaneity of the adsorption process. The positive ΔH suggests the endothermic nature of the adsorption.

1. Introduction

There are a number of liquid processes and waste streams at nuclear facilities that require treatment for process chemistry control reasons and/or the removal of radioactive contaminants. Cesium and cobalt are the most abundant radionuclides in nuclear fission products that are routinely or accidentally released. They have a relatively long half-life of about 30 years and are considered as hazardous elements for the environment (El-Naggar et al., 2008). Different techniques such as chemical precipitation, ion exchange, and evaporation are used for the treatment of aqueous waste solutions containing these ions. Ion exchange has become one of the most commonly used treatment methods for hazardous and radioactive aqueous streams due to its simplicity, selectivity, and efficiency. A wide range of materials having different chemical and physical properties, which can be naturally occurring or synthetic, is available for this technique. Inorganic ion exchange materials have arisen as an increasingly important replacement or complement for conventional organic ion exchange resins, particularly in liquid radioactive waste treatment due to their radiation stability and greater selectivity for certain radiological important species, such as cesium and cobalt. In the last decade, the natural clay minerals, such as montmorillonite (Mt) (Deng et al., 2017), kaolinite (Ekosse, 2010), and palygorskite (attapulgite) (Galan, 1996), are widely used in catalysis, as adsorbents (Hashemian and Shahedi, 2013), in composites (Zhang et al., 2016), in sensors (Darder et al., 2005), electrode (Kenfack et al., 2005), as antibacterial materials (Morrison et al., 2016) and in nuclear waste treatment and storage (El-Kamash, 2008). Surface modification of clay minerals has become very important for improving the practical applications of clays and clay minerals, Surface modification by polymers is found to be one of the most effective methods, as the surface properties can be widely changed by a variety of functional polymers. The composite polymers based on the co-polymer mixture of poly acrylamide-acrylic acid have much better swelling properties as compared to the single monomer (acrylamide and acrylic acid monomers), this is referenced, and the clay minerals are added to enhance their adsorption capacity (Liu et al.). The present work deals with the preparation and characterization of poly (acrylamide-acrylic acid)/kaolin composite and a series of experiments to assess the utility of this prepared composites for the removal of Cs^+ and Co^{2+} ions from aqueous solutions under batch conditions. The relevant data, with respect to kinetic and equilibrium of the adsorption and exchange of Cs^+ and Co^{2+} ions, have been obtained using simple kinetic and thermodynamic models.

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* Corresponding author.
E-mail address: emanelmasry74@gmail.com (E.H. EL-Masry).

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2. Experimental

2.1. Materials

Chemicals and the reagents used were of high purity and the solutions were synthesized using distilled water. Acrylamide, Acrylic acid, *N*, *N′*-methylene bisacrylamide (DAM) and acetone were purchased from Merck. Egyptian kaolin was obtained from El-Nasr Company. The pH of the solution was adjusted using 0.1 mol/L H_2SO_4 and/or NaOH which was purchased from Fluka. Cesium and Cobalt were supplied as cesium chloride and, Cobalt chloride, from Sigma–Aldrich Company.

2.2. Preparation

All the preparations were performed using de-oxygenated bi-distilled water; under a stream of pure dry nitrogen at room temperature. Polyacrylamide (PAM), was prepared by gamma radiation-initiated polymerization of 10% acrylamide monomer solution using gamma radiation at a dose 10 kGy. (P(AM-AA)/K) was prepared by mixing (1%) DAM aqueous solution with P(AM) gel (3%) in presence of 0.1 g kaolin. The mixture was stirred vigorously at room temperature for about 2H. After that, AA (10% aqueous solution) was added. Finally, the dispersion was irradiated at the present temperature and a dose of 20 kGy. After irradiation the solidified samples were precipitated in acetone, dried, analyzed and cut into small pieces (El-Zahhar et al., 2005).

2.3. Characterization of the prepared polymer/clay composite

FT-IR spectra were analyzed using the disc technique. The sample was thoroughly mixed with KBr as a matrix. The spectra were recorded at a wavelength of 500–4000 cm^{-1} on a spectrometer model system 2000 FT-IR, Perkin Elmer Co., USA. The pellet was made by mixing KBr with fine powder of the composite samples (10:1 mass ratio of KBr to composite). FTIR analysis was applied on poly (acrylamide-acrylic acid)/kaolin, composite loaded with Cs ions and composite loaded with Co ions.

X-ray diffraction spectra of Kaolin before and after composite preparation were taken using X-ray powder diffractometer (Philips Analytical PW-1710) equipped with Cu Kα radiation at a scanning speed of 2°/min from 10° to 90° operated at voltage 40 kV and applied potential current 30 mA.

The Morphology of the composite polymer powder was recorded using Scanning Electron Microscopy (SEM). The composite sample was washed, dried and mounted on the support and then made conductive with sputtered gold. The surface morphology was carried out using Philips XL 30 attached with EDX Unit.

Shimadzu TGA–DTA system of type TGA-DTA-50, Japan was used for the measurements of the weight losses and the phase changes of the sample, respectively. The heating rate was 10 °C/min in the presence of nitrogen gas to avoid thermal oxidation of the powder sample.

2.4. Adsorption investigations

2.4.1. Swelling studies

In order to determine the swelling behavior, 1 g of the dry composite was placed into distilled water and kept at a room temperature. The swollen composite was periodically removed and weighted after removing the excess water on composite surface with filter paper (Chen et al., 2016; Zaharia et al., 2015). The weight ratios of dry and swollen samples were recorded. The water content of the swollen composites and components were calculated using the following expression (Huang et al., 2012):

$$\text{Swelling ratio (\%)} = [(w_f - w_o)/w_o] \times 100 \quad (1)$$

where w_o and w_f are the weight of composite before and after swelling, respectively.

2.4.2. Effect of pH

Adsorption of Cs^+ and Co^{2+} ions by (P(AM-AA)/K) was studied as a function of pH keeping other parameters fixed. For determination of the optimum pH value, a series of 50 mL bottles each containing 0.1 g of the composite polymer and 10 mL of 10^{-4} metal ion solution were shaken overnight to be sure that the equilibrium was attained at room temperature. The values of the initial pH of the solutions were adjusted to range from 1.0 to 8.0. The obtained dispersion was centrifuged at 6000 rpm. The concentrations of Cs^+ and Co^{2+} ions in the clear liquid phases were determined and the percentage removal, U%, is calculated according to the following formula:

$$U\% = \frac{C_o - Ce^*}{C_o} 100 \quad (2)$$

where C_o and C_e are the initial and equilibrium concentrations (mmol/L) of the metal ion in solution.

2.4.3. Batch adsorption studies

Kinetic studies were managed by shaking a series of 10 mL of a solution containing 10^{-4} M of Cs^+ and Co^{2+} ions individually with 0.1 g of (P(AM-AA)/K) in a 50 mL stoppered bottle for different time intervals. The pH of the aqueous solution was adjusted to the optimum value pH 7. The dispersion obtained was centrifuged at 6000 rpm. The clear liquid phases were subjected to the elemental analysis using Atomic Absorption Spectrophotometer (Buck scientific model VGP 210).

2.4.4. Adsorption equilibrium experiments

Adsorption experiments were carried out using the batch technique. 0.1 g of P(AM-AA)/K was placed in a set of 50 mL glass-stoppered bottles and 10 mL of different concentrations, from 10^{-4} M to 5×10^{-2} M, Cs^+ and Co^{2+} ions individually. The pH of the dispersion was adjusted to the desired value (pH = 7) then the mixture was shaken for 3 h. The experiments were also conducted at three different temperatures (298, 313 and 333 K) using an initial ion concentration of 10^{-4} M. The concentration of each metal ion in the liquid phase was determined. The amount of metal ion adsorbed at equilibrium, q_e (mmol/g), is calculated using the following Eq. (3)

$$q\ (\text{mmol/g}) = \frac{(C_o - C_e)V}{m} \quad (3)$$

where V is the volume of solution in liter and m is the weight of adsorbent in gram.

3. Results and discussion

3.1. Characterization of the prepared material

The FT-IR spectra of P(AM-AA)/K, Fig. 1, illustrated some slightly shifted characteristic peaks of acrylamide, such as the intense broad band at 3435 cm^{-1} which was assigned to the H_2O molecules and N—H-stretching vibration of acrylamide units, which overlapped with the OH vibrations of the Kaolin (El-Zahhar et al., 2014; Zhang and Wang, 2007), the band at 1032 cm^{-1} is assigned to the Si—O—Si stretching vibration of kaolin (Zaharia et al., 2015). The band at 1732 cm^{-1} is attributed to the stretching vibrations of carboxylate groups and the band at 1401 cm^{-1} is characteristic to the CO stretching vibration of carboxylate groups (Borai et al., 2015). The absorption band at 2963 cm^{-1} is assigned to hydrogen-bonded —OH of the carboxylic group (Zaharia et al., 2015; Mushtaq et al., 2014), $-CH_2$ and $-CH_3$ group. The characteristic band of amide group in acrylamide units was found at 1540 cm^{-1} (Hadizade et al., 2017), the bands at 1253 and 1166 cm^{-1} are characteristic for C—N stretching of the amide group and the band at 580 cm^{-1} is attributed to OCN stretching of