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Adsorption of manganese ion using polyaniline and it's nanocomposite: Kinetics and isotherm studies

Milad Hallajiqomi[a,*], Hossein Eisazadeh[b]

[a] Faculty of Chemical, Petroleum and Gas Engineering, Semnan University, Semnan, Iran
[b] Chemical Engineering Department, Shomal University, P.O. Box 731, Amol, Iran

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ABSTRACT

In this research, the preparation of polyaniline (PAn) nanocomposite as adsorbent and it's capability in manganese removal was investigated. The PAn nanocomposites were prepared using different kind of surfactants such as hydroxypropylcellulose (HPC), poly (vinyl pyrrolidone) (PVP), poly (vinyl alcohol) (PVA) and poly (ethylene glycol) (PEG) in the presence of KIO_3 as an oxidant. The products were characterized in terms of morphology and chemical structure with scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). Batch studies were performed to evaluate the influence of various experimental parameters including pH, adsorbent dosage, and contact time. Optimum conditions for manganese removal were found to be pH 10, adsorbent dosage of 10 g/L and equilibrium time 30 min. Also, the kinetic of adsorption system have been studied based on the assumption of pseudo-second order rate law. The experimental results have been analyzed using a pseudo-Langmuir adsorption isotherm and a pseudo-Freundlich adsorption isotherm models. The Freundlich adsorption isotherm model was found to represent the measured sorption data better than Langmuir adsorption isotherm. According to the evaluation using the pseudo-Freundlich model, the monolayer adsorption capacity (q_{max}) of PAn for manganese ions was obtained to be 50.251 mg/g.

Introduction

The discharge of heavy metal pollutants into the environment from sewage, industrial and mining waste effluents is a serious problem due to its impact on human health and natural environment. These numerous metal ions such as Zn^{2+}, Cr^{3+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Hg^{+}, and so forth are non-biodegradable. On the other hand, conducting polymers such as PAn and polypyrrole (PP) exhibit excellent electrical conductivities and outstanding thermal stability, while their chemical solubility and mechanical properties are poor leading to a reduced processability [1,2]. To overcome these difficulties, most research efforts were focused on the chemical functionalization of such conducting polymers and on the composites of conducting polymers with elastomers [2,3].

The conduction process in PAn and PP has been explained by hopping of electrons along the polymeric chain [3,4], within the so-called Variable Range Hopping (VRH) [5] description.

The composites of conducting polymers such as PAn with noble metals are useful application in electrocatalysis, catalysis, removal of heavy metals, recovery of noble metals, and design of fuel-cell electrodes, sensors, and conducting printing inks [5–7].

PAn is one of the most important conducting polymers because of its high environmental stability, low cost and reversible control of its conductivity [8].

The term heavy metal refers to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. Examples of heavy metals that are harmful to humans include arsenic, cadmium, chromium, copper, lead, mercury, nickel and manganese. Chronic exposure to these metals can have serious health consequences. Humans are exposed to heavy metals through inhalation of air pollutants, consumption of contaminated drinking water, exposure to contaminated soils or industrial waste, or consumption of contaminated food. Food sources such as vegetables, grains, fruits, fish and shellfish can become contaminated by accumulating metals from surrounding soil and water [9–11].

Heavy metal exposure causes serious health effects, including reduced growth and development, cancer, organ damage, nervous system damage, and in extreme cases, death. Exposure to some

* Corresponding author. Fax: +98 2333354120.
E-mail address: miladsos313@chmail.ir (M. Hallajiqomi).

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metals, such as mercury and lead, may also cause the development of autoimmunity, in which a person's immune system attacks its own cells. This can lead to joint diseases such as rheumatoid arthritis, and diseases of the kidneys, circulatory system, and nervous system [12–14].

Soluble manganese (Mn) is often found in considerably greater concentrations in mine drainage waters than in unpolluted streams and groundwater. Even though there are uncertainties regarding the toxicity of manganese, recent research has shown that elevated concentrations of manganese are highly correlated to the toxicity of lake sediment pore water [15–17].

The main purpose of this paper is the removal of manganese ion by using adsorption and determining the ability of PAn, PAn/HPC, PAn/PEG, PAn/PVA and PAn/PVP nanocomposite to remove the manganese ion from aqueous solution. Also effects of pH, adsorbent dosage and contact time have been investigated.

Experimental

Materials and methods

All reagents were analytical pure grade and used as received without further purification, unless stated otherwise. Aniline monomer and HPC (with an average molecular of weight 106 g/mol) were supplied from Aldrich. Monomer of Aniline was purified by simple distillation method. Sodium dodecylbenzenesulfonate (DBSNa) was obtained from Loba chemie. Other materials used in this work such as PVP (with molecular weight of 25,000 g/mol), PVA (with molecular weight of 72,000 g/mol), PEG (with molecular weight of 35,000 g/mol), sodium dodecylhydrogensulfonate (DHSNa), and KIO_3 were purchased from Merck. Distilled water was used throughout this work. Mn (II) ions were prepared by solving $Mn(NO_3)_2{\cdot}4H_2O$ in water and used as inlet feed solution. SEM model XL30, FTIR spectrometer model shimadzu 4100, inductively coupled plasma (ICP) model vista-pro and also pH meter model pH 211 were employed.

PAn preparation

In order to prepare PAn nanocomposite, 1 g KIO_3 was added to 100 mL of sulphuric acid (1 M) and mixed completely using magnetic stirrer until the uniform solution was resulted. After 30 min, 1 mL fresh distilled aniline monomer was added to aqueous solution. The reaction was carried out for about 5 h at room temperature. The resulted polymer was filtered via filter paper in order to separate oligomers and impurities. Finally, product was washed several times with distilled water and dried at room temperature [18].

Synthesis of PAn nanocomposite

KIO_3 was used as the oxidant, whereas other materials such as DBSNa, DHSNa, HPC, PVA, PVP and PEG were used as surfactants. The reaction was carried out in an aqueous media at room temperature for 5 h. The conditions for composite formation are summarized in Table 1.

In a typical experiment, 1 mL of aniline monomer was added to 100 mL stirred aqueous solution of sulfuric acid (1 M) containing 0.2–0.4 g of one of the surfactants. After 5 h, polymer composite was filtered and washed several times with deionized water to separate the oligomers and impurities. Finally, the product was dried at room temperature.

Experimental procedure

All adsorption experiments were performed by a completely mixed batch reactor (CMBR). In order to remove manganese from aqueous phase, 50 mL of solution was added to the beaker containing desired adsorbent. At the end of process intervals, the sorbate was filtered and the concentration of manganese ion was determined. The experimental runs were carried out twice and the results of the mean values of adsorbed manganese ions concentrations were measured and reported. The wastewater was synthesized by adding $Mn(NO_3)_2{\cdot}4H_2O$ into the distillated water to produce the synthetic wastewater with Mn^{2+} concentration of 100 mg/L. Also, experimental variables such as initial concentration of manganese ions 100 mg/L; contact time between PAn and manganese ion solution 5–60 min; pH 3–13; dosage of PAn/surfactant adsorbent 100–1000 mg/50 mL are considered in this study. The amount of adsorption at equilibrium, q_e (mg/g), was computed as follows:

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are the initial and equilibrium solution concentrations (mg/L), respectively, V is the volume of solution (L) and m is the weight of adsorbent (g).

Results and discussion

Characterization of PAn nanocomposite

Morphology

Fig. 1 shows SEM images of the PAn and PAn/PVP composites. Fig. 1(a) reveals a PAn structure of tiny particles in the form of clusters. These are smaller than those of PAn Homopolymers globules prepared under the same conditions but without the inorganic substrate. The coating with conducting polymer produced by surface polymerization is very visible. The coating of PVP has always been found to be uniform by visual inspection, while coating defects have been suspected in the case of PVP at low PAn Contents. Some PAn precipitate produced by the precipitation polymerization of aniline in the liquid phase adhered to the PAn coated PVP (Fig. 1(b)) when the polymerization proceeded at a high (0.2 M) concentration of aniline.

Table 1
The amount of surfactants used for the preparation of polyaniline nanocomposites.

Type of composite	Surfactant concentration (g/L)	Aniline (mol/L)	KIO_3 (g/L)
Polyaniline	–	0.107	10
Nanocomposite of PAn and PEG	2	0.107	10
Nanocomposite of PAn and PVP	2	0.107	10
	4	0.107	10
Nanocomposite of PAn and HPC	2	0.107	10
	4	0.107	10
Nanocomposite of PAn and PVA	2	0.107	10
Nanocomposite of PAn and DHSNa	2	0.107	10
Nanocomposite of PAn and DBSNa	2	0.107	10

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