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Study of the removal of Zn(II) from aqueous solution using polypyrrole nanocomposite

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ABSTRACT

Zinc is one of the most important pollutants for surface and ground water. Because of its acute Toxicity and non-biodegradability, zinc-containing liquid and solid wastes are considered as hazardous wastes. The aim of this research work is to investigate sorption characteristic of polypyrrole coated on the sawdust (PPy/SD) for the removal of Zn (II) ions from aqueous solutions. The sorption of Zn (II) ions by batch method is carried out. The optimum conditions of sorption were found to be: a PPy/SD dose of 0.5 g in 100 mL of Zn (II), contact time of 14 min, pH and temperature 3 and 40 °C respectively. It was found that temperature has a positive effect on the removal efficiency. Three equations, i.e. Morris–Weber, Lagergren and pseudo-second order have been tested to track the kinetics of removal process. The kinetic data indicated that the adsorption process was controlled by pseudo-second-order equation. The Langmuir, Freundlich and D–R are subjected to sorption data to estimate sorption capacity, intensity and energy. The data is fitted with Freundlich. The thermodynamic parameters ΔH, ΔS and ΔG are evaluated. Thermodynamic parameters showed that the adsorption of Zn (II) onto PPy/SD was feasible, spontaneous and endothermic under studied conditions. It can be concluded that PPy/SD has potential to remove Zn (II) ions from aqueous solutions at different concentrations. It was found that increasing the initial concentration causes decreasing in the ion removal. For the desorption experiments, several solvents (alkaline, bases and water) have been used. It was achieved 75% desorption efficiency using NaOH also PPy/SD has been used for the removal of Zn (II) from real waste water (plating wastewater and shows high efficiency in the zinc removal.

1. Introduction

The removal of toxic heavy metals from aqueous streams is an important issue facing industries discharging effluents bearing heavy metals. Zinc is an essential element but its concentration in air, water and food should be below the tolerance limits, otherwise it would be harmful to humans and animals [1]. Many industries, especially electroplating, manufacturing batteries, pigments and ammunition production release continuously Zn(II) in wastewaters [2]. Too much intake of Zn(II) can lead to respiratory incapacitation, as indicated by increased respiratory activity such as breathing rate, volume and frequency of ventilation, coughing, decrease in oxygen uptake efficiency [3].

Various treatment processes have been introduced for the removal of metal ions [4]. Current treatment processes include precipitation, oxidation/reduction, membrane filtration/ osmosis, ion exchange and adsorption. Each process has its advantages and disadvantages, but ion exchange/adsorption methods do offer the most direct method of producing the highest quality treated water [5].

Activated carbon is a commonly used adsorbent for the removal of pollutants present in water and wastewater the high cost of activated carbon has restricted its more widespread use. A variety of natural sorbents has been exploited for the sorption of toxic metal ions from aqueous systems [6–9].

Since the discovery of conducting polymers three decades ago, a large volume of research work has been performed associated with the physics and chemistry of conducting polymers. PAn is one of the most environmentally stable known conducting polymer and also one of the most commonly investigated conducting polymer due to its high electrical conductivity and ease of preparation [10]. Conducting polymer find applications in various fields such as microelectronics, composite materials, optics and biosensors [11] and as adsorbent [12,13]. The ion exchange capacities of conducting polymers were well understood and it was found to depend on the polymerization conditions, the type and size of the dopants incorporated during the polymerization process as well as on the ions present in the electrolyte solution, the polymer thickness and ageing of the polymer [14]. Review of the literature revealed that polypyrrole synthesized in

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solutions with small dopants such as Cl^-, ClO_4^-, NO_3^-, etc., mainly exhibits anion-exchanger behavior due to the high mobility of these ions in the polymer matrix. While under certain conditions cation exchange was also found to take place with large dopants like polyvinylsulfonate and polystyrenesulfonate, due to immobility of these ions in the polymer matrix [15]. adsorption of metal ions by several functionalized polymers based on amines derivatives such as polyacrylonitrile fibers, ethylenediamine, polyacrylamides, poly-4-vinylpyridine, polyethyleneimine, aniline formaldehyde condensate, etc., have been reported [16–20]. Chakraborty and coworkers have investigated one amine-based polymer, short-chain PAn coated on jute fiber for the removal of chromium in batch mode and Fixed-bed column [21,22]. Polypyrrole was used in the removal of fluoride ions from aqueous solution. In this study, an attempt was made to study the possibility of using conducting polypyrrole, with chloride ion as a dopant, for the removal of fluoride ions from aqueous solutions by batch sorption method [23].

This article reported the removal efficiency of Zn(II) from aqueous solution using PPy/SD and present isotherm equations. Also PPy/SD has been used for the removal of the Zn(II) from plating wastewater.

2. Materials and methods

2.1. Materials

A stock solution of Zn(II) (1000 mg/L) was prepared in milli-Q water with $ZnSO_4$. It was then diluted to prepare solutions of the desired concentrations. All the chemicals used throughout this study were of analytical grade either from Merck. pH of the solution was monitored by adding 0.5 M HCl and 0.5 M NaOH solution as per required pH value. Pyrrole (Merck) was purified by vacuum distillation for polymerization. Nylon 66, Mamrez tree sawdust (SD), Tarom rice husk (RC), a commercial grade of Activated carbon from coconut coir pith (AC), Purolite 302 (cation exchanger, a macroporous polyacrylic crosslinked with divinylbenzene, ROHM and HASS Co), and Amberjet (cation exchanger, a styrene divinylbenzene copolymer, ROHM and HASS Co), have been used as received (section 3.11).

2.2. Instrumentation

In this study, a scanning electron microscope ((SEM) model XL30) was used to characterize the surface of the PPy/SD at very high magnification. The PPy/SD was coated with gold and palladium by a sputter coater with conductive materials to improve the quality of micrograph. The thickness of the coating was 30.00 nm, and the density was 19.32 g/cm^3.

Functional groups in PPy/SD were determined by the Fourier transform infrared (FTIR) spectroscopy. Spectra were collected with a spectrometer using KBr pellets. In each case, 1.0 mg of dried PPy/SD sample and 100 mg of KBr are homogenized using mortar and pestle thereafter pressed into a transparent tablet at 200 kgf/cm^2 for 5 min. The pellets are analyzed with a FTIR Spectrometer (Shimadzu 4100) in the transmittance (%) mode with a scan resolution of 4 cm^{-1} in the range 3500−500 cm^{-1}.

Flame atomic absorption spectrophotometer (Model 929, Unicam) was used for the analysis of Zn(II) in aqueous solution. Concentrations were determined after calibrating the instrument with standards within the concentration range of 0.5–10 mg/L for Zn(II). To measure the unknown Zn(II) ions concentration in aqueous solution, we diluted the solution to bring the concentration within the calibration range. The light source was a hollow-cathode lamp of the element that was being measured.

The pH measurements of all aqueous samples were performed following standard methods with SP21 pH meter manufactured by VWR scientific product. The meter was standardized using buffer solutions with the following pH values: pH 4.0, pH 7.0 and pH 10.0.

2.3. Characterization of mamrez tree sawdust

Mamrez tree sawdust is a heterogeneous material consisting largely of small spheres, irregular, porous, coke like particles of cell wall of plant cells. Maple wood sawdust samples were collected from a local saw mill “Chobo kaghaz”, Shahi, Iran. The surface seems to be rough, and protrusions can be seen throughout the micrograph. Pores can be seen however, not extending into the matrix. The surface roughness is indicative of high surface area. Characteristics of the adsorbent such as surface area, bulk density, moisture content, ash content, and solubility in water (inorganic and organic matter) were determined. The results are summarized in Table 1.

2.4. Batch adsorption experiments

The adsorption experiments in this work were done for the study the effect of experimental conditions on Zn(II) adsorption and determining the conditions that achieve the maximum amount of chromium removal. Isotherm, kinetic and thermodynamic evaluations were also conducted in this portion of the study. The adsorption tests were conducted in magnetic mixer. The magnetic mixer was 300 rpm throughout the study with 100 mL of Zn(II) solution prepared from the dilution of 1 g/L stock solutions. At the end of predetermined time intervals, the sorbate was filtered and the concentration of Zn(II) was determined. All experiments were carried out twice and the adsorbed concentrations given were the means of duplicate experimental results. All the experiments were repeated twice, and the experimental error was below 4%, the average data were reported. In all experiments the PPy form was powder. The efficiency of Zn(II), % Removal, was calculated as:

$$\textit{Removal efficiency}(\%) = 100\frac{C_i - C_f}{C_i} \quad (1)$$

Where C_i is the initial concentration (mg L^{-1}) and C_f is the final concentration (mg L^{-1}). q is the amount of metal adsorbed per specific amount of adsorbent (mg/g).The sorption capacity at time t, q_t (mg/g) was obtained as follows:

$$q_t = (C_i - C_t) \times V / m \quad (2)$$

where C_i and C_t (mg/L) were the liquid phase concentrations of solutes at initial and a given time t, V was the solution volume and m the mass PPy (g).

The amount of adsorption at equilibrium, q_e was given by:

$$q_e = (C_i - C_e) \times V / m \quad (3)$$

Where Ce (mg/L) was the ion concentration at equilibrium.

Table 1
Various physical parameters for the adsorbent (mamrez tree sawdust).

Parameters	Values
Particle size (μm)	100–150
Surface area (m^2/g)	620
Bulk density (g/cm^3)	0.25
Moisture contents (%)	5.75
Water soluble components (inorganic matter) (%)	16.45
Insoluble components (organic matter) (%)	76.25