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Removal of Zinc Ions from Aqueous Solution Using Polyaniline Nanocomposite Coated on Rice Husk

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Abstract: In this research, the preparation of polyaniline (PAn)/ rice husk nanocomposite as adsorbent was discussed and the capability of adsorbing zinc is studied. The polyaniline nanocomposite was prepared in presence of KIO_3 as an oxidant, coated on rice husk ash via casting method. The morphology and chemical structure of absorbent evaluated by with scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR), respectively. Batch studies were performed to evaluate the influence of various experimental parameters such as pH, adsorbent dosage and contact time. Optimum conditions for zinc removal were found to be pH 3, adsorbent dosage of 10 g/L and equilibrium time of 20 minutes. The equilibrium adsorption isotherm was better described by Langmuir adsorption isotherm model. The adsorption capacity (q_{max}) of PAn/RH for zinc ions in terms of monolayer adsorption was 24.3 mg/g.

Key words: Polyaniline; Nanocomposite; Rice husk; Zinc Removal

INTRODUCTION

Water pollution by heavy metals remains as an important environmental issue in water. The import of heavy metals associated negatively with health and ecosystem [1]. Hence it becomes necessary to remove these toxic metal ions from municipal and industrial effluents to protect plants, animals and human beings from their adverse effect before discharging into natural water bodies. Although, several separation methods are available, but the process of adsorption is the most versatile and plays a significant role in removal of heavy metal contamination from water bodies [2-4]. Several polymers, clay minerals, dead biomass and metal oxides have been used as adsorbents [5-8]. Considerable attention was given in recent years for the removal of heavy metal toxic ions such as chromium, manganese, zinc, cadmium, zinc, etc. by polymeric beads [9, 10].

Conductive polymers such as polyacetylene, polyaniline, polypyrrole and polythiophene, have attracted many research interests in wide range applications such as rechargeable batteries [11], electromagnetic interference (EMI) shielding [12], antistatic coatings ([13], gas sensors [14], optical devices [15] removal of heavy metals [16, 17] and so forth. Conducting polyaniline is unique among conductive polymers on account of its excellent optical and electronic properties [18, 19].

Polyaniline has attracted considerable attention because of its unique electrical, optical and electrooptical properties and its numerous potential applications [20].

Conductive polyaniline (PAn) exhibits extraordinary electronic properties, such as low ionization potential and high electron affinity as a result; it can be easily reduced or oxidized. Because of such physical properties of PAn finds wide variety of applications in batteries, electromagnetic devices, biosensors, gas-separating membranes, electromagnetic shielding and as an antistatic material [21-24].

The main purpose of present research is the removal of zinc ion by using adsorption and determining the ability of PAn/RH nanocomposite to remove of zinc ion from aqueous media.

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Experimental

Instrumentation: A magnetic mixer (Helmer model MK20, Germany), digital scale (Helmer model FR 200, Germany), scanning electron microscope (SEM)) Philips model XL30, Netherland), fourier transform infrared (FT-IR) spectrometer (Shimadzu model 4100, Japan), oven (Binder model FD 23, USA) and an atomic fluorescence spectrophotometer (perkin-elmer Corp. model 2380, USA).

Reagents and Standard Solutions: All reagents were used as received without further purification, unless stated otherwise. Distilled deionized water was used throughout this work. Aniline monomer was purified by simple distillation. Materials used in this work were KIO_3, NaOH, HCl and sulphuric acid from Merck. Rice husk (RH) was collected from local rice mill (Mazandaran, Iran).

Polyaniline Preparation: For preparation of polyaniline, 1g KIO_3 was added to 100 mL of sulphuric acid (1M) and then uniform solution was resulted by using magnetic mixer. Then, 1 mL fresh distilled aniline monomer was added to stirred aqueous solution. The reaction was carried out for 5 h at room temperature. Consequently, the resulted polymer was filtered on filter paper in order to separate the oligomers and impurities, product was washed several times with deionized water and dried at temperature about 60°C in oven for 24 h.

Synthesis of Polyaniline/RH Nanocomposite: For preparation of Polyaniline/rice husk nanocomposite, 1 g KIO_3 was added to 100 mL of sulphuric acid (1N) and then uniform solution was resulted by magnetic mixer. After 30 min, 1 g of fine powder rice husk was added to solution and after 20 min, 1 mL fresh distilled aniline monomer was added to stirred solution. The reaction was carried out for 5 h at room temperature. Consequently, the product was filtered for the purpose or removal of the impurities, the product was washed several times with deionized water and dried at temperature about 60°C in oven for 24 h.

Method of Removal: Completely mixed batch reactor (CMBR) technique was used to remove of Zinc ions from water. A 100 mL of wastewater were added to the beaker containing of the desired adsorbent. At the end of predetermined time intervals, the sorbate was filtered and the concentration of zinc ions was determined. All experiments were carried out twice and the adsorbed zinc ions concentrations given were the means of duplicated experimental results. Experimental variables considered were concentration of Zn in water 100 ppm; contact time between PAn/RH nanocomposite with Zn ion solution 5–25 min; pH 2–12; and dosage of PAn/RH nanocomposite, 100–1000 mg/50 mL.

Atomic fluorescence spectrophotometer was used for the analysis of zinc ions in aqueous solution. Concentrations were determined after calibrating the instrument with standards within the concentration range of 0.5 –10 mg/L for zn. To measure the unknown zinc ions concentration in aqueous solution, the solution was diluted to bring the concentration within the calibration range. The light source was a hollow-cathode lamp of the element that was being measured.

RESULTS AND DISCUSSION

Characterization of Nanocomposite: Figs. 1 and 2 show SEM images of rice husk before and after coating with PAn. It can be seen that the surface of RH is covered with uniformly dispersed spherical PAn particles. Presumably, PAn particles are not only present on the surface of rice husk, but they can also be distributed throughout the interior of the RH, filling cavities. Fig. 3 shows with high magnificent of polymer coated on the rice husk. As can be seen, PAn has been formed. In general, increasing the amount of additives in the reaction, such as rice husk ash, influences the physical properties of product.

Figurer 4 shows the FTIR spectra of PAn/RH nanocomposites, in comparison with pure PAn, at 400 – 4000 cm^{-1} Peaks at 1566 and 1478 cm^{-1} corresponding to quinone and benzene slightly shifted ring-stretching deformations of PAn are also detected in the nanocomposite. The band at 1304 cm^{-1} belongs to the C–N stretching of a secondary aromatic amine strengthened by protonation of PAn and is also present in spectra of composite. Furthermore, the characteristic peaks of PAn are seen at 2926 cm^{-1} (N–H in benzenoid ring) and 800 cm^{-1} (out-of-plane deformations of C–H). These peaks can also be seen in the spectra of PAn/RH nanocomposites. All bands in nanocomposites were slightly shifted, which indicate that there is some interaction between PAn and the metal oxides of RH.

Effect of pH: In order to evaluate the influence of acidic and alkaline solution on the adsorption, the experiments were carried out in a wide range of initial pH ranging from 2 to 12. The experiment was performed by PAn/RH nanocomposite, with zinc ions concentration of 100 mg/L, at room temperature with contact time of 20 min. The results are shown in Fig. 5. Removal of zinc decreased with increasing pH of solution and a maximum value was reached at an equilibrium pH of around 3.

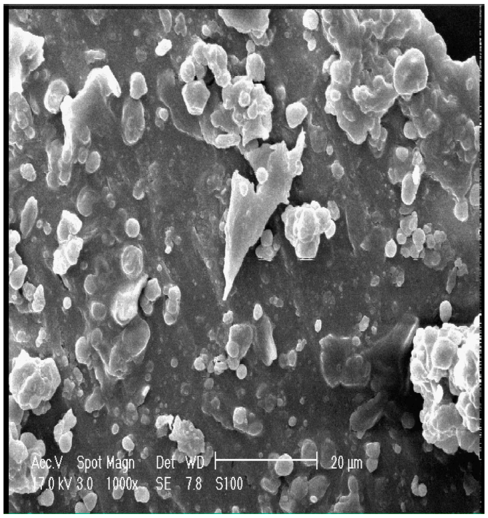

Fig. 1: SEM of untreated rice husk

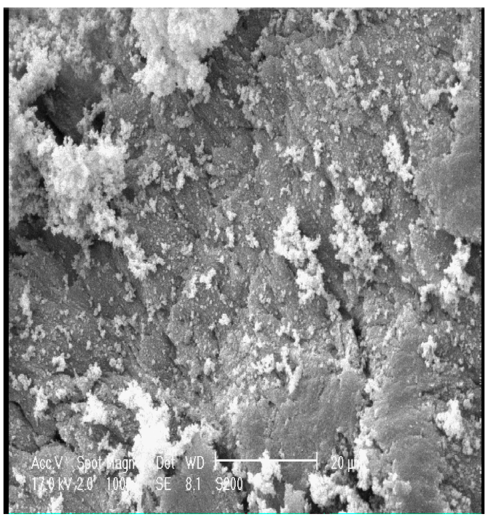

Fig. 2: SEM of PAn/RH generated in aqueous media. reaction conditions: (KIO_3=10 g/L, aniline monomer 10.75×10^{-2} mol/L, volume of solution 100 mL, reaction time 5 hours at room temperature)

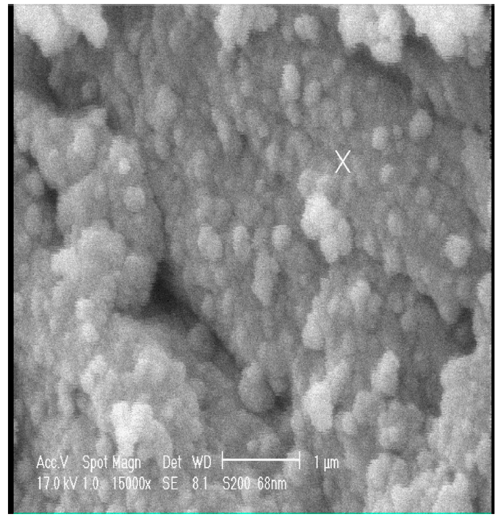

Fig. 3: SEM of PAn/RH with magnification of 15000

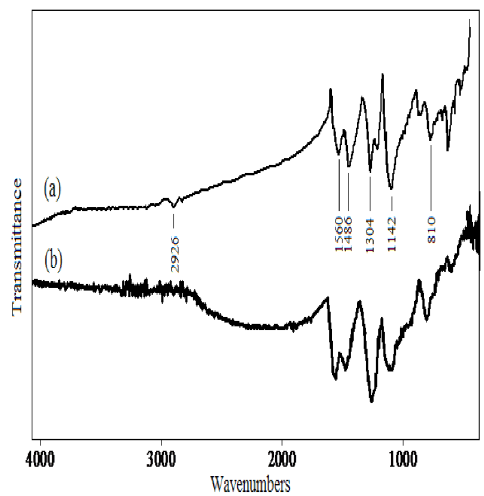

Fig. 4: FTIR spectra of: (a) PAn and (b) PAn/RH nanocomposite generated in aqueous media

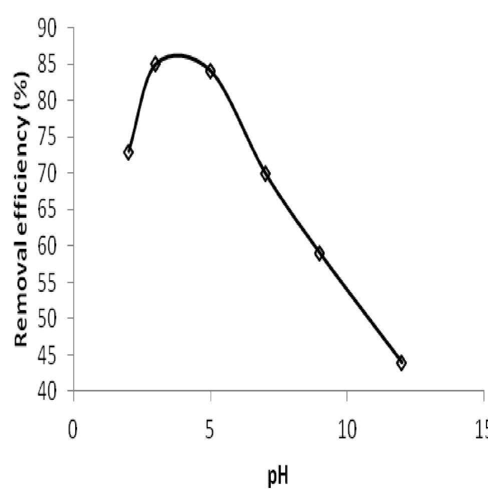

Fig. 5: The effect of pH on the removal efficiency PAn/RH

Effect of Adsorbent Dosage: The removal percentage of zinc was studied by adsorbent (PAn/RHA) dose between 100 and 1000 mg at zinc ions concentration of 100 mg/L. Results are presented in Fig. 6.

The Zn removal efficiency increases up to an optimum dosage beyond which the removal efficiency does not significantly change. This result was anticipated because of a fixed initial solute concentration, increasing adsorbent doses provides greater surface area and more adsorption sites, whereas the adsorbed metal ions quantity (q) per unit weight of the sorbent decreased by increasing the magnetic beads quantity.

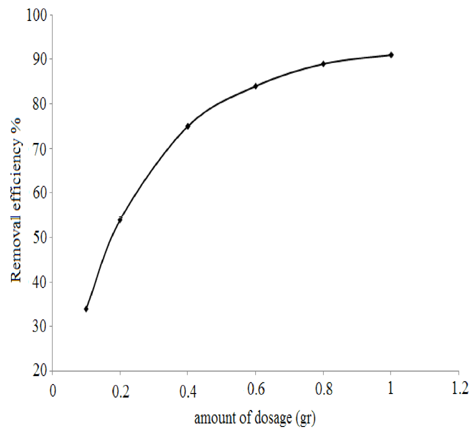

Fig. 6: The effect of adsorbent dosage on the removal efficiency with PAn/RH

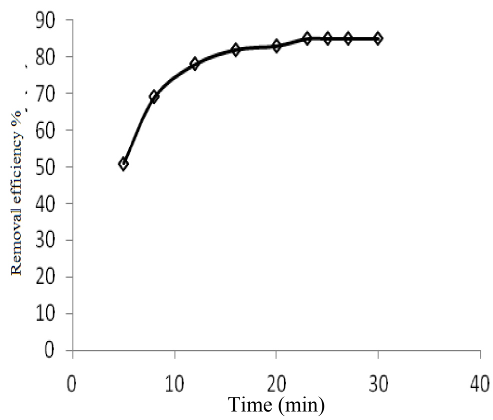

Fig. 7: The effect of contact time on the removal efficiency with PAn/RH

At very low adsorbent concentration, the absorbent surfaces become saturated with the metal ions and the residual metal ion concentration in the solution was high.

Effect of Contact Time: Fig. 7 shows the effect of contact time on sorption of zinc ions by PAn/ RH nanocomposite. For these cases, pH of 10 was used for zinc solution solution and zinc concentration in water was 100 mg/L. Also PAn/RH dose of 1 g in 100 mL were used. For Zn sorption rate reaches up to 91 by PAn/ RH nanocomposite, when contact time was 20 min and then little change of sorption rate was observed. This result revealed that adsorption of zinc was fast and the equilibrium was achieved after 20 min of contact time. Taking into account these results, a contact time of 20 min was chosen throughout experiments

Batch Adsorption Experiment: Adsorption experiments were performed by completely mixed batch reactor (CMBR) technique to remove zinc from water. A 50 mL of solution were added to the beaker containing of the desired adsorbent. At the end of predetermined time intervals, the sorbate was filtered and the concentration of zinc ion was determined. All experiments were carried out twice and the adsorbed zinc ions concentrations given were the means of duplicate experimental results. Experimental variables considered were initial concentration of zinc ions 100 mg/L; contact time between PAn/RH and zinc ion solution 5–25 min; pH 2–12; dosage of PAn/RH 100–1000 mg/50 mL. The amount of adsorption at equilibrium, (mg/g), was computed as follows:

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

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 (g) is the weight of adsorbent was used.

Adsorption Isotherms: The adsorption isotherm for the removal of zinc ion was studied using adsorbent dosage of between 100 and 1000 mg/50 mL at an initial concentration level of 100 mg/L. The adsorption equilibrium data are conveniently represented by adsorption isotherms, which correspond to the relationship between the mass of the solute adsorbed per unit mass of adsorbent (q_e) and the solute concentration for the solution at equilibrium (C_e).

Langmuir Adsorption Isotherm: The data obtained were fitted to Langmuir adsorption isotherm applied to equilibrium adsorption assuming monolayer adsorption onto a surface with a finite number of identical sites and is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (2)$$

Linear plot of Ce/q_e versus Ce was employed to determine the value of q_{max} (mg/g) and b (L/mg) (Fig. 8). The data obtained and correlation coefficients (r^2) were summarized in Table 1. Weber and Chakraborti expressed essential characteristics and the feasibility of Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) which can be defined in the following equation:

$$R_L = \frac{1}{1 + bC_0} \qquad (3)$$

The R_L values indicate the shape of the isotherm as follow:

R_L value	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0<R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 1: Langmuir and Freundlich adsorption isotherm constants for zinc ions on PAn/RH

Langmuir constants		Freundlich constants	
q_{max} (mg/g)	24.3	K_f ((mg/g)/(mg/L)$^{1/n}$)	1.958
b (L/mg)	0.037	n	2.02
r^2	0.983	r^2	0.8922
R_l	0.21		

The R_L value for the adsorption on PAn/RH is 0.21 and it revealed a favorable adsorption.

Freundlich Adsorption Isotherm: The adsorption data obtained were then fitted to the Freundlich adsorption isotherm, which is the simple known relationship describing the adsorption equilibrium and is expressed by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \quad (4)$$

A linear form of this expression is:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e$$

Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as of adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (5) using Freundlich plots as shown in Fig. 9. The values for Freundlich constants and correlation coefficients (r^2) for the adsorption process are also presented in Table 1. The values of n between 1 and 10 (i.e., 1/n less than 1) represent a favorable adsorption. The n values obtained for the adsorption process represented a beneficial adsorption.

Table 1 shows that experimental data were well fitted to Langmuir (r^2 = 0.983); but for Freundlich adsorption isotherm the fitted data were slightly scattered (r^2 = 0.892). Therefore uptake of zinc ions preferably follows the monolayer adsorption model.

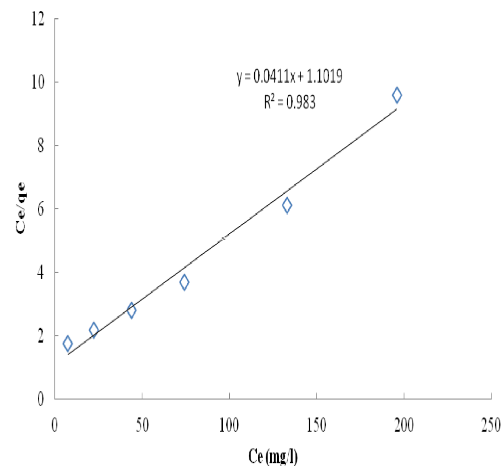

Fig. 8: Langmuir plot for the adsorption of zinc by PAn/RH: pH, 3; initial concentration, 100 mg/L; contact time, 20 min.

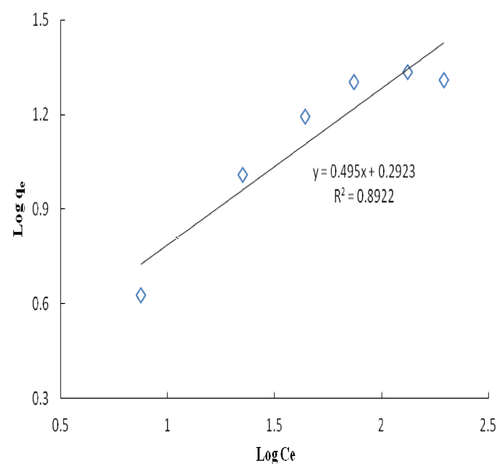

Fig. 9: Freundlich plot for the adsorption of zinc by PAn/RH: pH, 3; initial concentration, 100 mg/ L; contact time, 20 min.

CONCLUSIONS

In this study, polyaniline/rice husk nanocomposite was prepared by coating the rice husk substrate with aniline using the chemical oxidative polymerization method. The ability of adsorbent for the removal of zinc from aqueous media was investigated. The results indicate that, the Pan/RH nanocomposite has a considerable potential for the removal of Zn from water. Optimum conditions for zinc removal were found to be pH 3, adsorbent dosage of 10 g/L and equilibrium time of 20 min. In addition, Langmuir and Freundlich adsorption isotherm models were used to represent the experimental data.

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