

Removal of arsenic from aqueous solution using polyaniline/rice husk nanocomposite

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Abstract—The present study deals with the adsorption of arsenic ions from aqueous solution on polyaniline/rice husk (PAn/RH) nanocomposite. Batch studies were performed to evaluate the influence of various experimental parameters like pH, adsorbent dosage, contact time and the effect of temperature. Optimum conditions for arsenic removal were found to be pH 10, adsorbent dosage of 10 g/L and equilibrium time 30 minutes. Adsorption of arsenic followed pseudo-second-order kinetics. The equilibrium adsorption isotherm was better described by Freundlich adsorption isotherm model. The adsorption capacity (q_{max}) of PAn/RH for arsenic ions in terms of monolayer adsorption was 34.48 mg/g. The change of entropy (ΔS^0) and enthalpy (ΔH^0) was estimated at -0.066 kJ/(mol K) and -22.49 kJ/mol, respectively. The negative value of the Gibbs free energy (ΔG^0) indicates feasible and spontaneous adsorption of arsenic on PAn/RH.

Key words: Polyaniline, Rice Husk, Nanocomposite, Arsenic, Isotherm

INTRODUCTION

Arsenic is one of the most toxic and carcinogenic chemical elements and is regarded by the World Health Organization as the first priority issue among the toxic substances [1]. Various technologies are currently available to remove arsenic from water, such as ion exchange [2], coagulation (coprecipitation) [3], reverse osmosis [4], bioremediation [5], and adsorption [6,7]. Adsorption is a common practice for arsenic removal from drinking water due to technological and cost advantages.

Conducting polymers have become one of the most attractive subjects of investigation in the last few decades. Their unique properties such as electrical conductivity and electrochemical properties (like metals), mechanical strength and ease of processing (like polymers) and possibility of both chemical and electrochemical synthesis, make them useful in wide area of applications. Among these polymers, polyaniline (PAn) is unique because of its high electrical conductivity, good environmental stability and ease of preparation [8]. In this regard some studies have focused on electrochemical interaction of conducting polymers with toxic metals [9,11]. Results of these studies have led to the application of conducting polymers in analysis [11,14] and abatement [15,17] of some toxic metals from the environment. However, to the best of our knowledge, nothing has been reported on the preparation of polyaniline/rice husk composites by in situ chemical polymerization of aniline. Rice husk is agricultural waste, accounting for about one-fifth of the annual gross rice, 545 million metric tons, of the world. Rice husk contains abundant floristic fiber, protein and some functional groups such as carboxyl, hydroxyl and amidogen [18], which make the adsorption processes possible. And it has been successfully used to remove colored component [19], metal ions [20] from water.

The capacity of PAn/RH to remove arsenic ions from aqueous solution is comparable with other adsorbents. Although, direct comparison of PAn/RH with other adsorbents is difficult, owing to the different applied experimental conditions. It was found that the adsorption capacity of PAn/RH (34.48 mg/g) for arsenic ions is comparable with other adsorbents and in fact greater than certain adsorbents reported earlier. The amounts of arsenic ions removed per unit mass by various adsorbents (in mg/g) are: Ferruginous manganese ore, 0.537 [21]; Ferruginous manganese ore, 19.11 [22]; Granular ferric hydroxide, 0.11 [23]; Polymetallic sea nodule, 0.69 [24]; Ferrihydrite, 5.63 [25]; Nanocrystalline titanium dioxide, 59.94 [26]; Mesoporous alumina, 47.2 [27] and Polyaniline-sawdust, 1.56 [28].

Therefore, in this study, an attempt was made to study the possibility of using conducting polyaniline/rice husk nanocomposite, for the removal of arsenic ions from aqueous solutions by batch sorption method.

MATERIALS AND METHODS

1. Instrumentation

The concentration of arsenic in solution was determined on an atomic fluorescence spectrophotometer (2380, PerkinElmer Corp.). The detection limit of the instrument was $1 \mu\text{g/L}$. The pH was measured using pH meter (HANNA 211) and The SEM (VEGA, TESCAN) images and FT-IR (Shimadzu 4100) spectra were obtained from Razi Metallurgical Research Center, Tehran.

2. Chemicals and Reagents

All the reagents used were of commercially available high purity. The aniline was purchased from Aldrich and was distilled prior to use. Stock solutions of arsenic were prepared by dissolving arsenic (As_2O_3) chlorid (Merck) in doubly distilled water. Ammonium peroxydisulfate (APS); poly(vinyl pyrrolidone) (PVP, Mw=25,000) and hydrochloric acid (HCl) were obtained from Merck (Schuchardt, Germany). Rice husk (RH) was collected from local rice mill, Mazan-

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daran, Iran.

3. Polyaniline/Rice Husk Preparation

A weighed amount of rice husk was suspended in 80 ml of 1 M HCl containing 0.5 g of PVP, and then aniline (0.1 M) was injected into this suspension which was stirred magnetically for 1 h. Then 20 ml of oxidant solution (0.05 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$) gradually (in 10 minutes) was added to the mixture which was stirred for a further 5 h. The precipitated composite was filtered off and rinsed with 1 M HCl and distilled water and then it was dried at room temperature. The composites are abbreviated as PAN/RH.

4. Batch Adsorption Experiment

Adsorption experiments were performed by completely mixed batch reactor (CMBR) technique to remove arsenic from water. A 50 mL of solution was added to the beaker containing the desired adsorbent. At the end of predetermined time intervals, the sorbate was filtered and the concentration of arsenic ion was determined. All experiments were performed twice and the adsorbed arsenic ions concentrations given were the means of duplicate experimental results. Experimental variables considered were initial concentration of arsenic ions 100 mg/L; contact time between PAN/RH and arsenic ion solution 5-60 min; pH 3-13; dosage of PAN/RH 125-1,000 mg/50 mL. The amount of adsorption at equilibrium, (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 (g) is the weight of adsorbent was used.

RESULTS AND DISCUSSION

1. Characterization of PAN/RH Nanocomposite

1-1. FTIR Spectroscopy

Fig. 1 shows the FTIR spectra of PAN/RH composites, in comparison with that of pure PAN, at 400-4,000 cm^{-1} . Peaks at 1,566 and 1,478 cm^{-1} corresponding to quinone and benzene slightly shifted ring-stretching deformations of PAN are also detected in the nanocomposite. The band at 1,304 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 2,926 cm^{-1} (aromatic C-H stretching) and 800 cm^{-1} (out-of-plane deformations of C-H) [29]. These

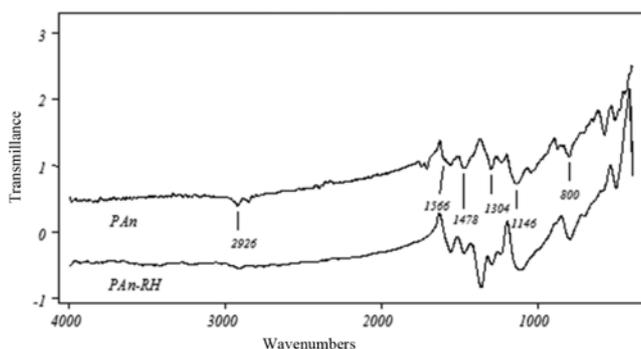


Fig. 1. FTIR spectra of PAN and PAN/RH nanocomposites.

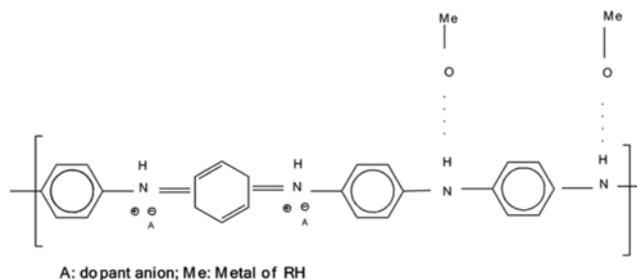


Fig. 2. Schematic structure showing hydrogen bonding interaction between PAN and RH.

peaks can also be seen in the spectra of PAN/RH composites. All bands in composites are slightly shifted, which indicates that there is some interaction between PAN and the metal oxides of RH.

It is well known that in systems with polyaniline, strong guest-host interactions, such as hydrogen bonding, occur in the form of $\text{NH}\cdots\text{O}$ -metal in an inorganic matrix. Consequently, the frequency shift of C-N at 1,343 cm^{-1} in PAN/RH composite systems is attributed to interaction between PAN and RH (i.e. $\text{NH}\cdots\text{O}$ hydrogen bonding), which is schematically depicted in Fig. 2.

Polyaniline has a reactive N-H group in a polymer chain flanked on either side by a phenylene ring, imparting a very high chemical flexibility. It undergoes protonation and deprotonation in adsorption at nitrogen which has a lone pair of electrons. Protonation of PAN not only involves the ingress of protons, but it also accompanied by ingress of anions, to maintain charge neutrality. This suggests that the behavior of PAN depends on the pH and on the counterion of the Bronsted acid used for doping.

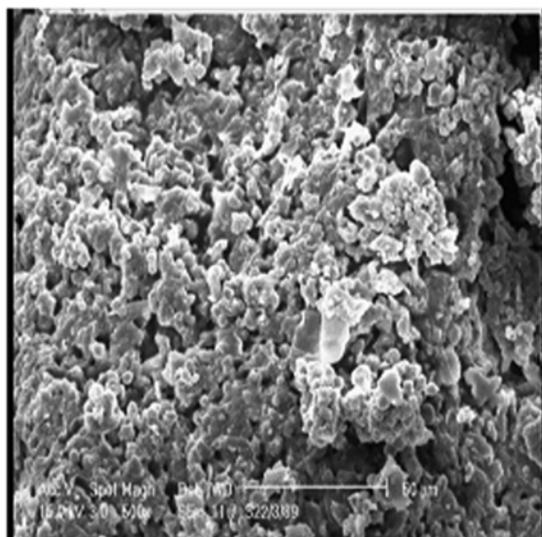
1-2. Morphology

Fig. 3 shows SEM images of the RH and PAN/RH composites. In pristine RH spherical particles with average size about 5 μm are visible (Fig. 3(a)). Fig. 3(b) reveals a PAN structure of tiny particles in the form of clusters. Figs. 3(c) show the SEM images of the PAN/RH composites. It can be seen that the surface of RH is covered with uniformly dispersed rice grain PAN particles. These are smaller than those of PAN homopolymer globules prepared under the same conditions but without the inorganic substrate. 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, as reported by Ray and Biswas for ZrO_2/PAN composite [30].

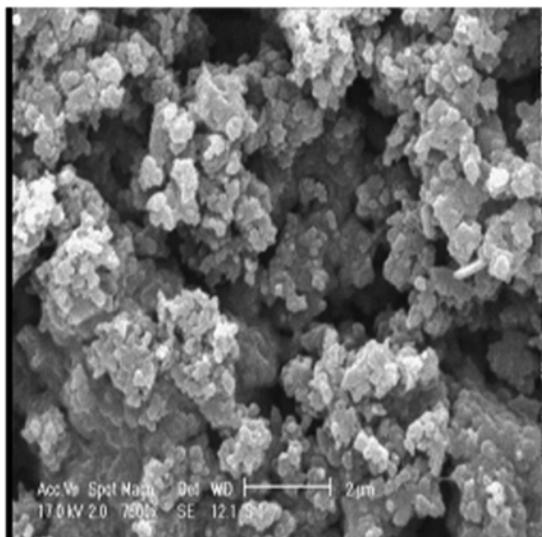
2. Effect of Medium pH

The pH of the solutions has been identified as the most important variable governing metal adsorption. This is partly due to the fact that hydrogen ions themselves are strong competing ions and partly that the solution pH influences the chemical speciation of the metal ions as well as the ionization of the functional groups onto the adsorbent surfaces. The pH of the solution affects the charge on the surface of the adsorbents, so the change in pH also affects the adsorption process and the H^+ ion concentration may react with the functional groups on the active sites on the adsorption surface.

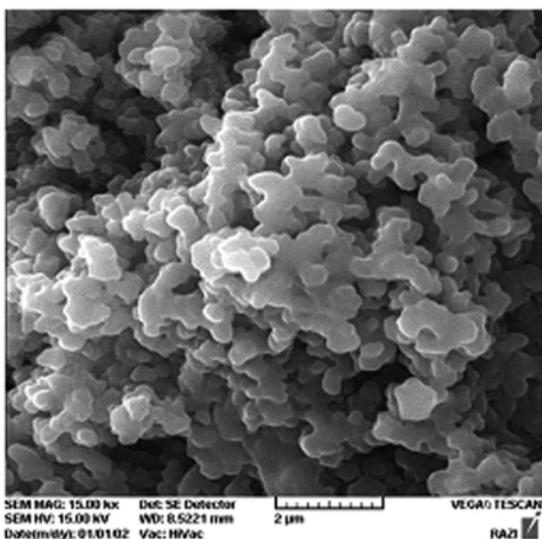
To evaluate the influence of this parameter on the adsorption, the experiments were carried out at different initial pH (3-14) values. The effect of pH on adsorption efficiencies is shown in Fig. 4. Removal of arsenic increases with increasing solution pH and a maximum value was reached at an equilibrium pH of around 10. The



(a)



(b)



(c)

Fig. 3. SEM micrographs of (a) RH; (b) PAn and (c) nanocomposite of PAn/RH.

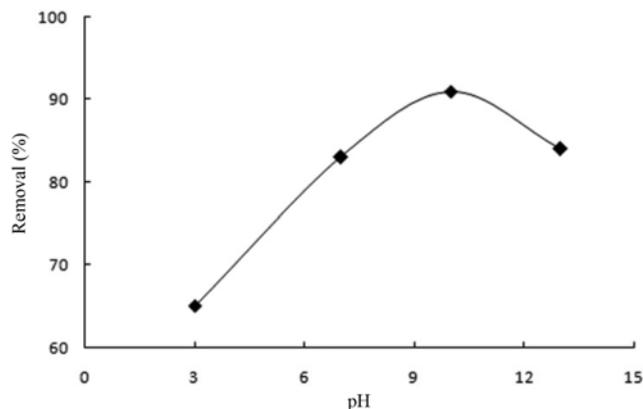


Fig. 4. Effect of pH on the adsorption of arsenic: initial concentration, 100 mg/L; contact time, 30 min.

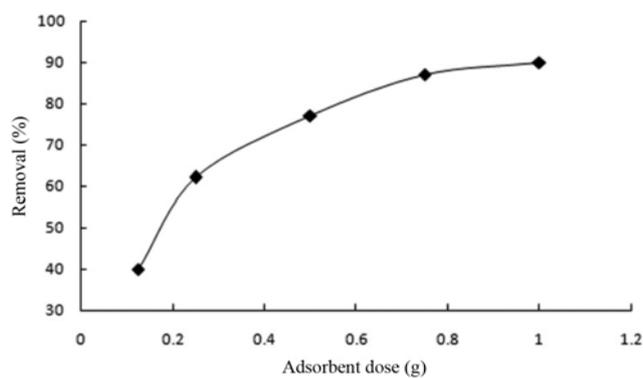


Fig. 5. Effect of adsorbent dosage on the removal of arsenic by PAn/RH: pH, 10; initial concentration, 100 mg/L; contact time, 30 min.

arsenic adsorption could be responsible for a complexation between arsenic ions and the nitrogen atoms of the $-N=C-$ groups through sharing their one lone pair of electrons.

3. Influence of Sorbent Dosage

The percentage removal of arsenic was studied by varying the adsorbent dose between 125 and 1,000 mg at an arsenic ions concentration of 100 mg/L (Fig. 5). The arsenic removal efficiency increases up to an optimum dosage beyond which the removal efficiency does not significantly change. This result was anticipated because for a fixed initial solute concentration, increasing adsorbent doses provides greater surface area (or adsorption sites), whereas the adsorbed metal ions quantity (q) per unit weight of the sorbent decreased by increasing the magnetic beads quantity.

4. Adsorption Isotherms

The adsorption isotherm for the removal of arsenic ion was studied using an adsorbent dosage of between 125 and 1,000 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).

4-1. Langmuir Adsorption Isotherm

The data obtained were then fitted to the Langmuir adsorption isotherm [31] applied to equilibrium adsorption assuming monolayer

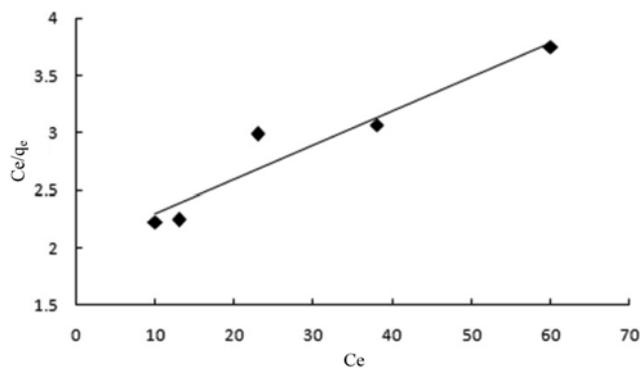


Fig. 6. Langmuir plot for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; contact time, 30 min; adsorbent dosage, 10 g/L.

Table 1. Langmuir and Freundlich adsorption isotherm constants for arsenic ions on PAN/RH

Langmuir constants		Freundlich constants	
q_{max} (mg/g)	34.48	$K_f((\text{mg/g})/(\text{mg/L})^{1/n})$	0.9
b (L/mg)	0.014	n	1.41
r^2	0.924	r^2	0.990
R_L	0.4		

adsorption onto a surface with a finite number of identical sites and is represented as follows:

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

A linear plot of C_e/q_e versus C_e in Fig. 6 was employed to determine the value of q_{max} (mg/g) and b (L/mg). The data obtained with the correlation coefficients (r^2) was listed in Table 1. Weber and Chakraborti [32] expressed the essential characteristics and the feasibility of the Langmuir isotherm in terms of a dimensionless constant separation factor or equilibrium parameter (R_L) which can be defined as:

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

The R_L value indicates the shape of the isotherm as follows [33].

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

The R_L value for the adsorption on PAN/RH is 0.4 and it revealed a favorable adsorption.

4-2. Freundlich Adsorption Isotherm

The adsorption data obtained were then fitted to the Freundlich adsorption isotherm [34], which is the earliest relationship known describing the adsorption equilibrium and is expressed by the following equation:

$$q_e = K_f C_e^{1/n} \quad (4)$$

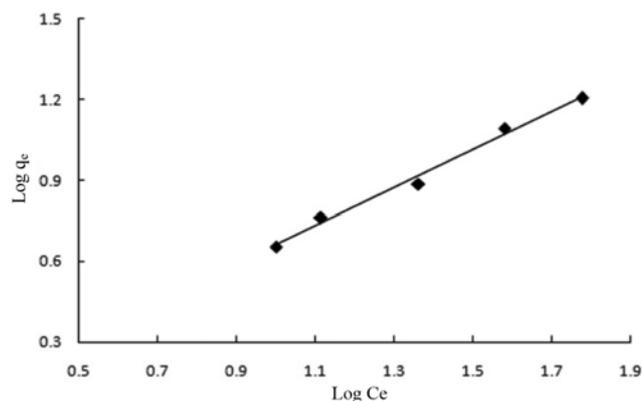


Fig. 7. Freundlich plot for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; contact time, 30 min; adsorbent dosage, 10 g/L.

A linear form of this expression is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

The Freundlich isotherm constants K_f and n are constants incorporating all factors affecting the adsorption process such as adsorption capacity and intensity of adsorption. The constants K_f and n were calculated from Eq. (5) using Freundlich plots as shown in Fig. 7. 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.

As can be seen in Table 1, experimental data are better fitted to the Freundlich ($r^2=0.990$) than the Langmuir ($r^2=0.924$) adsorption isotherm. Therefore uptake of arsenic ions preferably follows the heterolayer adsorption process.

5. Effect of Contact Time

The effect of contact time between PAN/RH and adsorbate is depicted in Fig. 8. It is evident that equilibrium was reached within 30 min, suggesting the possible multilayer coverage of arsenic ions on the surface of the adsorbent. This might be because once a certain

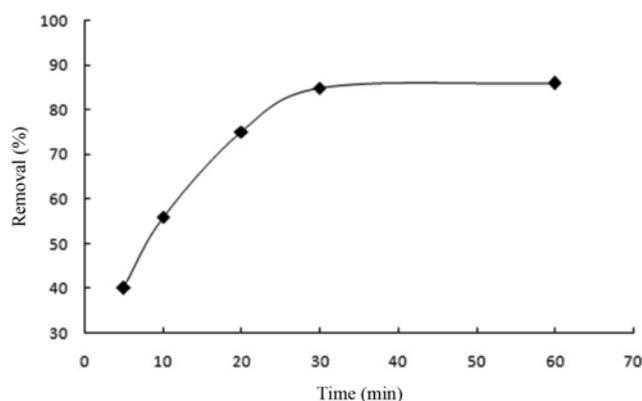


Fig. 8. Effect of contact time for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; adsorbent dosage, 10 g/L.

amount of arsenic ions get adsorbed onto PAN/RH within a given time (<30 min), no more removal occurs afterwards. To examine the mechanism of adsorption process such as mass transfer and chemical reaction, a suitable kinetic model is needed to analyze the rate data. Many models such as homogeneous surface diffusion model and heterogeneous diffusion model (also known as pore and diffusion model) have been extensively applied in batch reactors to describe the transport of adsorbate inside the adsorbent particles [35, 37]. The conformity between experimental data and the model predicted values was expressed by the correlation coefficient (r^2 , values close or equal to 1). A relatively high r^2 value indicates that the model successfully describes the kinetics of arsenic adsorption.

6. Adsorption Kinetics Study

6-1. Pseudo First-order Model

The sorption kinetics may be described by a pseudo first order equation [38-40]. The differential equation is the following:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{6}$$

After integration by applying the initial conditions $q_t=0$ at $t=0$ and $q_t=q$ at $t=t$ equation becomes:

$$\log\left(\frac{q_e - q_t}{q_e - q_0}\right) = \frac{k_1}{2.303}t \tag{7}$$

Eq. (7) can be rearrangement to obtain a linear form:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{8}$$

Where q_e and q_t are amounts of arsenic adsorbed at equilibrium and at time t (mg/g), respectively, and k_1 is the equilibrium rate constant of pseudo first-order adsorption, (1/min). Fig. 9 shows a plot of linearization form of pseudo first-order model at favorite concentration studied. The slopes and intercepts of plots of $\log(q_e - q_t)$ versus t were used to determine the pseudo first-order constant k_1

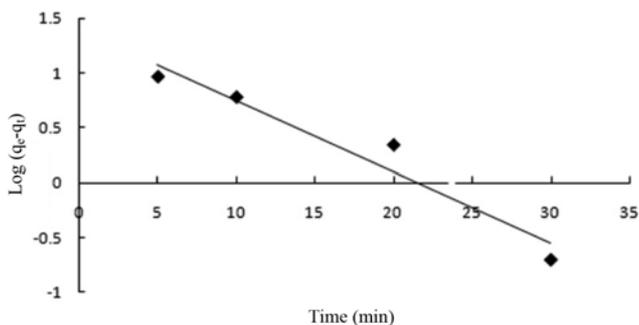


Fig. 9. Pseudo first-order plot for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; adsorbent dosage, 10 g/L.

Table 2. Comparison of the pseudo first-order and second-order adsorption and calculated experimental q_e

	Pseudo first-order	Pseudo second-order	
K_1 (1/min)	0.149	k_2 (g/min · mg)	0.0079
q_{exp} (mg/g)	25.4	q_{exp} (mg/g)	19.6
r^2	0.943	r^2	0.995

and equilibrium adsorption density q_e . However, the experimental data deviated considerably from the theoretical data. A comparison of the results with the correlation coefficients is shown in Table 2.

6-2. Pseudo Second-order Model

The adsorption kinetics may also be described by a pseudo second-order equation [40]. The differential equation is the following:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{9}$$

Integrating the equation and applying the boundary conditions gives:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k_2t \tag{10}$$

Eq. (10) can be rearranged to obtain a linear form:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{1}{q_e}t \tag{11}$$

Where k_2 is the equilibrium rate constant of pseudo second-order adsorption (g/mg · min).

The slopes and intercepts of plots of t/q_t versus t were used to calculate the pseudo second-order rate constants k_2 and q_e . The straight lines in plot of t/q_t versus t (Fig. 10) show good agreement of experimental data with the pseudo second-order kinetic model. Table 2 lists the computed results obtained from the pseudo second-order kinetic model. The calculated q_e values also agree very well with the experimental data. These indicate that the adsorption system studied belongs to the second order kinetic model.

7. Adsorption Thermodynamics

7-1. Effect of Temperature on Adsorption of Arsenic

To study the effect of temperature, adsorption experiments were done at 20-40 °C at an optimum pH value of 10 and adsorbent dosage of 10 g/L. The equilibrium contact time for adsorption was main-

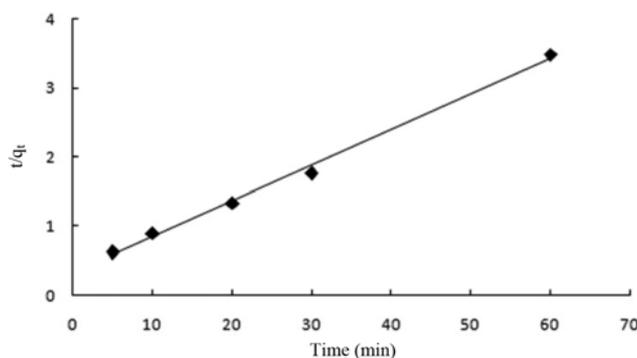


Fig. 10. Pseudo second-order plot for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; adsorbent dosage, 10 g/L.

Table 3. Equilibrium constants and thermodynamic parameters of PAN/RH

Temperature (°C)	K_c	$-\Delta G$ (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol)
20	3.34	2.94		
30	2.39	2.13	-22.49	-66.82
40	1.85	1.50		

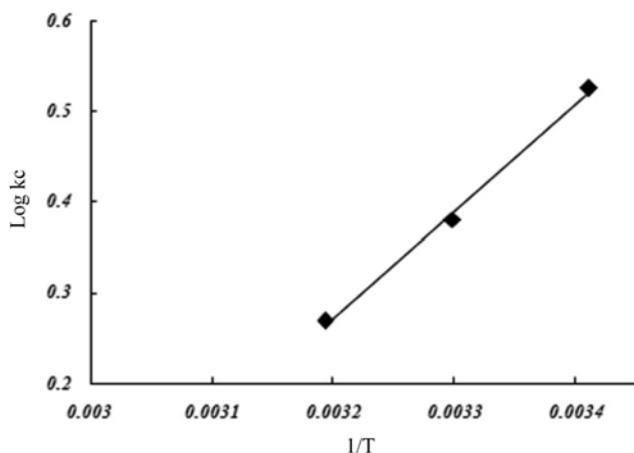


Fig. 11. Variation in the extent of adsorption with respect to temperature for the adsorption of arsenic by PAN/RH: pH, 10; initial concentration, 100 mg/L; contact time, 30 min; adsorbent dosage, 10 g/L.

tained at 30 min. The results are shown in Table 3 which shows the exothermic nature of the adsorption process that later was utilized for determination of changes in Gibbs free energy (ΔG^0), heat of adsorption (ΔH^0) and entropy (ΔS^0) of the adsorption of arsenic ions from aqueous solutions. By increasing temperature, the adsorption decreases; it may be due to the weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and between the adjacent molecules of the adsorbed phase.

7-2. Effect of Temperature on Thermodynamics Parameter

The thermodynamic parameters reflect the feasibility and spontaneous nature of the process. Thermodynamic parameters such as free energy, enthalpy and entropy can be estimated using equilibrium constants changing with temperature. Thermodynamic parameters were calculated using the following equations:

$$K_c = \frac{F_e}{1 - F_e} \quad (12)$$

Where F_e is the fraction of arsenic ions sorbed at equilibrium.

$$\log K_c = \frac{-\Delta H}{2.303RT} + \frac{\Delta S}{2.303R} \quad (13)$$

$$\Delta G = -RT \ln K_c \quad (14)$$

From the slope and intercept of the plot (Fig. 11), the values of ΔH^0 and ΔS^0 were computed, while ΔG^0 was calculated using Eq. (14). The values of these parameters are recorded in Table 3. It may be concluded from the negative value of ΔH^0 that the sorption process is exothermic. The negative values of ΔG^0 indicated that the removal of arsenic ions by PAN/RH is a spontaneous process.

CONCLUSIONS

Polyaniline/rice husk composites were prepared by coating the rice husk substrate with aniline in 1 M HCl solution using the chemical oxidative polymerization method. FTIR results confirm the presence of PAN in the structure of the composite. Globules of PAN grown on the RH surface are much smaller than those of PAN homopoly-

mer prepared under the same conditions but without substrate. Moreover, PAN/RH composites prepared using this cheap waste substrate can be used as new type of adsorbent for further preparation of adsorbent with polymeric matrices.

Batch adsorption experiments were performed for the removal of arsenic ions from aqueous solutions. The adsorption characteristics were examined at different pH values, contact time and adsorbent dosage. The results can be summarized as follows:

(1) The pH experiments showed that the governing factors affect the adsorption characteristics of all adsorbents are competition of the H^+ ions with metal ions at low pH values, maximum adsorption at pH 10. The arsenic adsorption could be responsible for a complexation between arsenic ions and the nitrogen atoms of the $-N=C-$ groups through sharing their four lone pairs of electrons.

(2) Increasing in mass of adsorbent leads to increase in metal ions adsorption due to increase the number of adsorption sites. Maximum uptake was obtained at adsorbent dose of 10 g/L, which may be considered as optimum adsorbent dosage level at the specified conditions.

(3) The equilibrium time for adsorption of arsenic ions from aqueous solutions was achieved within 30 min of contact time.

(4) The experimental data were better described by pseudo second-order model as evident from the correlation coefficient (r^2).

(5) The Freundlich adsorption isotherm model better represented the experimental data.

(6) Thermodynamic parameter studies show that the arsenic adsorption was spontaneous. The values of ΔH^0 and ΔS^0 were found to be -22.49 kJ/mol and -0.066 kJ/(mol K), respectively. The negative values of ΔH^0 indicate the exothermicity the process.

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