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Design of experiment for treatment of arsenic-contaminated water using Schiff's base metal complex modified Amberlite XAD-2

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ABSTRACT

The present study aims to develop a method using multivariate design of experiment approach for the treatment of arsenic-contaminated water. A newly synthesized resin i.e. Amberlite XAD-2 modified with Schiff's base-iron complex is used as a solid surface for the removal optimization. The Schiff's base was synthesized by simple condensation reaction and its Fe(III) complex was prepared by refluxing Fe(III) salt with methanolic solution of Schiff's base. XAD-2 was impregnated with Fe(III)-Schiff's base complex, and FTIR spectroscopy was used to characterize the complex. Individual and interactive effects of pH, time, concentration, and sorbent amount on removal of arsenic were studied using factorial design approach. A face-centered Draper–Lin composite design predicted 100% removal efficiency at optimum variables; pH 5.5, concentration of arsenic 10 mg L^{-1}, sorbent amount 57 mg, and shaking time 160 min. A good agreement between experimental and predicted data was observed. Langmuir and Frendlich sorption isotherms showed the validity of model with the sorption capacity of 227 µ mol^{-1} g and 85.9 mmol g^{-1}, respectively. Sorption energy calculated from D–R adsorption isotherm was 12 kJ mol^{-1} and corresponded to the possible ion exchange nature of the sorption process. The kinetics of removal of arsenic has also been investigated.

Keywords: Design of experiment; Modified XAD; Arsenic removal; Schiff's base resin; Water treatment

1. Introduction

Earth's crust contains arsenic as a widely dispersed element which exists at an average concentration of approximately 5 mg kg^{-1} [1]. Arsenic is considered as a potent endocrine disruptor and drinking arsenic-rich water over a long period leads to arsenic poisoning or arsenicosis [2]. WHO recommended limit of arsenic in water has been reduced to 5–10 µg L^{-1}. However, the total arsenic contamination in ground water, above the recommended level, has been reported in various countries such as India (3,700 µg L^{-1}) Mexico, Mongolia, Argentina (3,810 µg L^{-1}) Germany, Bangladesh (1,000 µg L^{-1}), Thailand, Chile, USA, Canada, China, Hungary (5,800 µg L^{-1}), Vietnam, Romania, Nepal, Myanmar, and Cambodia [3]. The arsenic contamination has been considered as a major public

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health issue, as it is classified as a group A and category 1 human carcinogen by the US Environmental Protection Agency (US EPA 1997) and the International Association for Research on Cancer (IARC 2004), respectively [4]. Due to its severe toxic effects on human health, its removal from water prior to use is recommended.

Techniques such as coagulation/precipitation, reverse osmosis, ion exchange, and adsorption are reported to effectively lower the concentration of arsenic in aqueous solutions [5,6]. Among the above-mentioned techniques, adsorption has been emerging as a significant technique for the removal of pollutants from aqueous systems. Various materials have been reported as an effective adsorbent including polymer resins, which have proved to be more selective by nature for the removal of metal ions [7–14]. Among number of chelating adsorbents reported for the removal of different metal ions [15,16] there are only a few which focus on the removal of arsenic [17–19].

The majority of adsorption studies have been carried out using classical univariant factors optimization in the batch mode. Classical optimization is time-consuming and it is not possible to study interaction effects of variables which could lead to false optimization values. These drawbacks can be overcome by the design of experiment. This study presents a very simple method for the preparation of modified resin and its potential for the treatment of arsenic-contaminated water. Intellectual effect of shaking time, initial concentration of As(V), pH, and sorbent amount on treatment efficiency is studied by response surface methodology.

2. Materials and methods

2.1. Apparatus and reagents

Aanalyst 800 (Perkin Elmer), Atomic Absorption spectrophotometer coupled with FIAS 100 was used for the determination of concentration of arsenic. Shaking Incubator (Model 1-40000) Irmeco GmbH (Geesthacht/Germany) was used for the batch sorption experiments. Fourier transform infrared (FT-IR) spectrometer (Thermo Nicolet IS-10 with diamond accessory) was used to record the IR spectra. Digital pH meter (Hanna 211, Germany) equipped with a combined glass calomel electrode was used for the pH measurements.

2.2. Synthesis of sorbent

Schiff's base (bis-acetylacetone-ethylene diimine) was prepared by dissolving acetylacetone and ethylenediamine in ethanol in a 2:1 ratio. The solution was warmed on water bath for 60 min and cooled at 0˚C for 12 h. Filtered product (Fig. 1) was recrystallized from methanol. Iron Schiff's base complex was obtained by refluxing Schiff's base and iron(III) salt solutions in methanol at 70˚C for 3 h. Amberlite XAD-2 was impregnated with 0.5% Schiff's base metal complex solution in methanol by stirring it with 1 g of XAD-2. The Amberlite XAD-2 (pore diameter 90–50 Å, bead size 200–400 mesh, and surface area 300–750 $m^2 g^{-1}$) was purchased from Fluka, Switzerland.

2.3. Batch sorption study

Batch sorption experiments were performed by taking weighed amounts of sorbent (10–100 mg) and 20 mL of solution containing 10–100 mg $L^{-1}$of As(V) ions maintained at pH 2–9. The mixture was shaken for 10–180 min at 100 rpm, while temperature was kept constant at 30˚C.

Removal efficiency was calculated by using Eq. (1):

$$\% \text{ removal} = \frac{C_0 - C_e}{C_0} \times 100 \tag{1}$$

where C_0 and C_e are the initial and final concentrations (mg L^{-1}) of Arsenic(V) ions.

2.4. Factorial design experiments

For the sorptive removal of arsenic from aqueous system, a design of 18 experiments was formulated

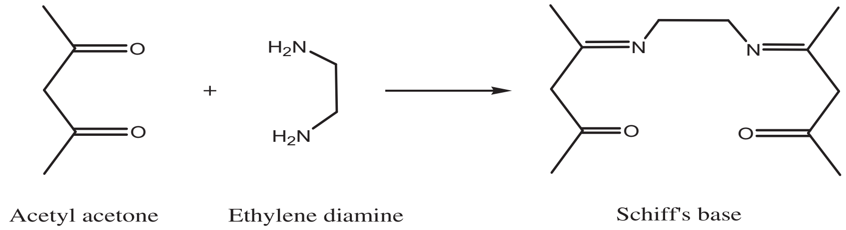

Fig. 1. Reaction scheme for the synthesis of acetylacetone-ethylenediamine.

using face-centered Draper–Lin small composite design. The range and levels of factors used in this study are shown in Table 1. Each factor was coded with −1, 0, +1, respectively, for minimum, mean and maximum value of investigated factor.

3. Results and discussion

3.1. Characterization by FTIR

In order to confirm the formation of Schiff's base and its metal complex, FT-IR study was carried out. Fig. 2(a) shows the FT-IR spectrum of Schiff's base, the bands at 1,513–1,563 cm^{-1} could be attributed to the stretching vibrations of C=N and C=O moieties (Fig. 1), respectively, which confirmed the formation of Schiff base. Fig. 2(b) shows the FT-IR spectrum of Iron-Schiff's base complex, the band at 1,513 cm^{-1} could be attributed to the stretching vibration of C=N moiety. The decrease in intensity of band at 1,563 cm^{-1} confirmed the participation of C=O moiety in Iron-Schiff's base complex. Fig. 2(c) shows FT-IR spectra of XAD-2 plain (a) and XAD-2 impregnated with Fe-Schiff base complex (b). The appearance of bands at 1,516 and 1,580 cm^{-1} could be attributed to the stretching vibrations of C=N and C=O moieties, respectively, which conformed the physical incorporation of Iron-Schiff's base complex onto the surface of XAD-2.

Table 1
Levels of factors used in experimental design for removal of As(V)

Independent variable	Coded levels −1	0	+1
Amount, A (mg)	10	55	100
Concentration (mg L^{-1}), B	10	55	100
pH, C	2	5.5	9
Time, (min.), D (x_4)	10	95	180

3.2. Parameter optimization through factorial design

Most of the studies reported on removal studies have used classical method of parameter optimization, in which one parameter is varied by keeping others at some constant value. In this method of optimization, interaction effect of parameters cannot be measured and hence it is hard to investigate the true optimum values of parameters affecting the adsorption efficiency. To overcome this problem, a DoE was used to study the intellectual effect of variable parameters. Draper-Lin composite design comprises 18 runs was used to develop a method for correlation between arsenic solution and variables such as pH, amount, concentration, and time. The DoE is shown in Table 2 along with predicted and experimentally calculated % removal values. A good correlation between experimental and predicted values can be evaluated by the values of R^2 and R^2_{adj} which are 99.98 and 99.92%, respectively.

3.3. Interpretation of residual graph

Residual plot i.e. the plot of difference between experimental and fitted values from the regression was examined to assess the fit of applied linear model to the obtained data. Fig. 3 shows that the experimental points are reasonably aligned with first

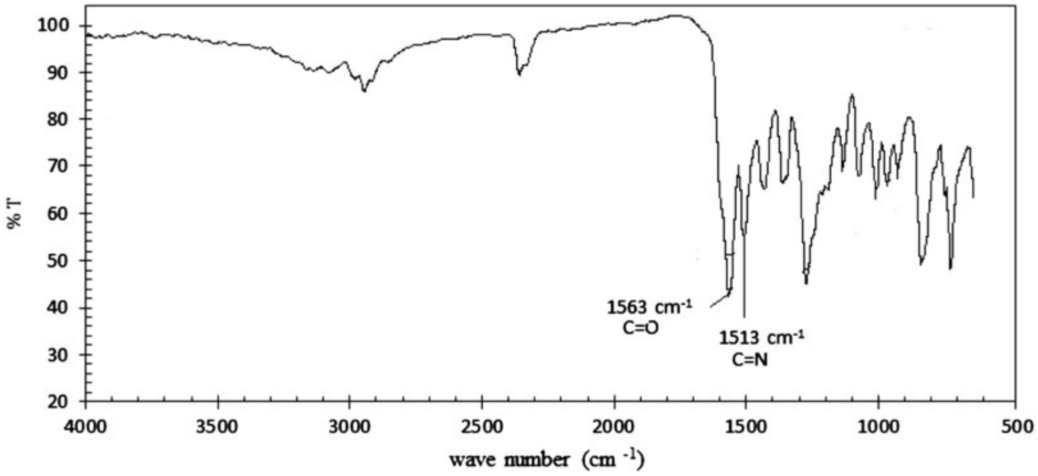

Fig. 2(a). FT-IR spectrum of Schiff base.

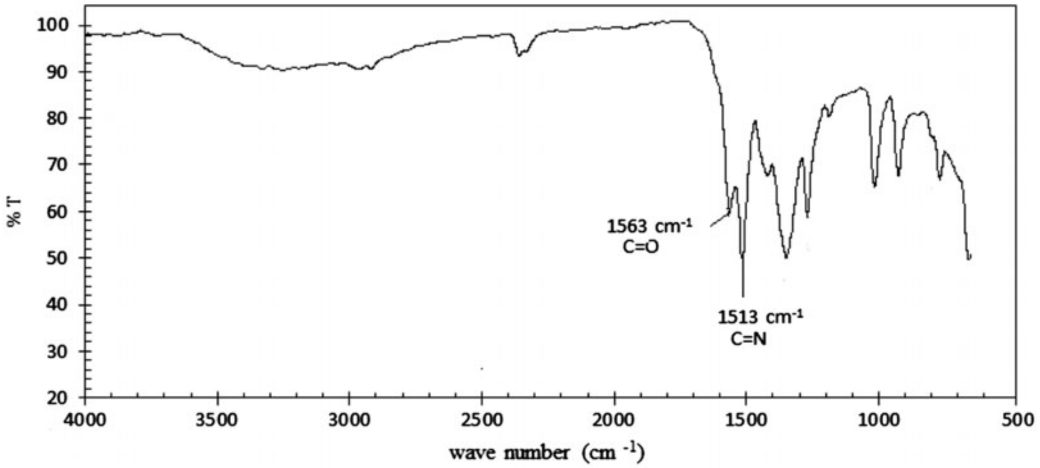

Fig. 2(b). FT-IR spectrum of iron Schiff base complex.

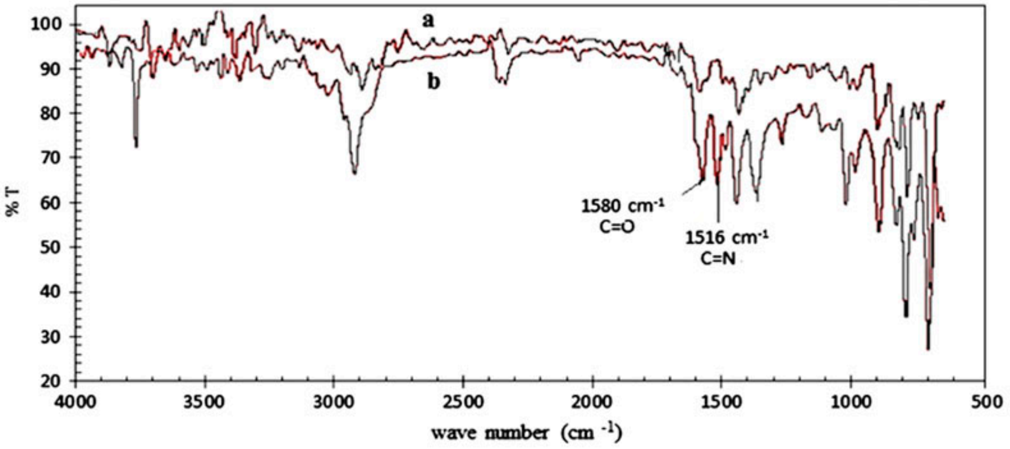

Fig. 2(c). FT-IR spectra of XAD-2 plain (a) and XAD-2 impregnated with Fe-Schiff's base.

two negative values followed by two positive values and again negative values and so on. This random pattern shows the suitability of a linear regression model.

3.4. *Student's* t*-test*

Significance of calculated effects was determined by Student's *t* test at 95% confidence level and is given as Pareto chart (Fig. 4). The *t*-value was found to be equal to 2 as shown in Fig. 4 by a vertical line. All the values presenting an absolute value higher than 2, which are located right of the line, are significant. The positive and negative signs, respectively, show the direct and inverse effect of studied terms on percentage removal of arsenic. Fig. 4 shows that there is a significant direct effect of time and interaction term amount and concentration on removal of arsenic by modified adsorbent, whereas a significant inverse relationship between pH and percentage removal is evident.

3.5. *Response surface plots*

In RSM, the best response range can be obtained from the three-dimensional response surface plots (Fig. 5(a)–(c)). Fig. 5(a) shows the combined effect of amount of adsorbent and the agitation time on removal efficiency of arsenic at optimum pH (5.5) and concentration (10 mg L^{-1}). The removal efficiency

Table 2
Experimental design and results for the removal of arsenic

Trial	Coded values				% Removal (Predicted)	% Removal (Experimental)
	A	B	C	D		
1	−1	−1	+1	−1	55.4	55.6
2	−1	−1	−1	−1	66.8	66.7
3	0	+1	0	0	50.2	50.0
4	+1	+1	−1	−1	50.1	50.0
5	+1	+1	+1	−1	49.8	50.0
6	0	0	0	−1	25.2	25.0
7	−1	+1	+1	+1	49.8	50.0
8	+1	0	0	0	3.2	3.0
9	0	0	+1	0	2.7	2.0
10	+1	−1	+1	+1	66.5	66.7
11	0	0	−1	0	5.7	6.0
12	+1	−1	−1	+1	66.8	66.7
13	−1	+1	−1	+1	50.1	50.0
14	0	−1	0	0	79.2	79.0
15	−1	0	0	0	2.2	2.0
16	0	0	0	+1	50.2	50.0
17	0	0	0	0	17.4	18.0
18	0	0	0	0	17.4	17.9

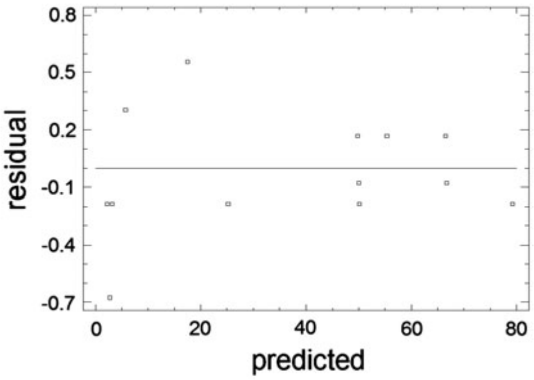

Fig. 3. Plot of residuals for the removal of arsenic by modified XAD-2.

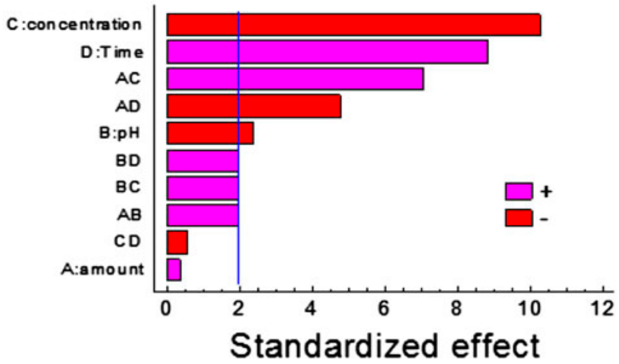

Fig. 4. Pareto chart for the removal of arsenic by modified XAD-2.

increased with increasing agitation time, whereas only slight change in removal efficiency can be seen with change in amount of adsorbent dose. The combined effect of pH of adsorbate solution and agitation time is plotted in Fig. 5(b). An increase in percentage removal with increasing agitation time can be seen from the figure, whereas percentage removal showed a decrease with increasing pH. Fig. 5(c)–(d) shows combined effect of concentration with pH and time, respectively. A decrease in percentage removal can be seen with increasing initial concentration of solution.

3.6. Regression analysis

Regression analysis helps to understand that how the typical value of the dependent variables undergo a change when any one of the independent variables is varied, while the other independent variables are taken constant. In Table 3, p-value is defined as the smallest level of significance leading to the rejection of null hypothesis. The significance of any coefficient term can be estimated by the magnitude of F and p, the larger the magnitude of F and smaller the value of p, the more significant is the corresponding coefficient term [20]. Table 3 shows the F values of variables as:

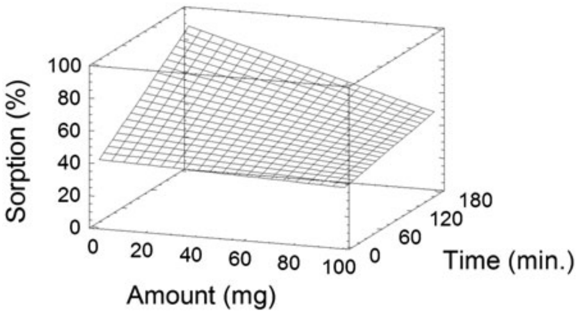

Fig. 5(a). Response surface plots for interaction effect of time and amount on removal.

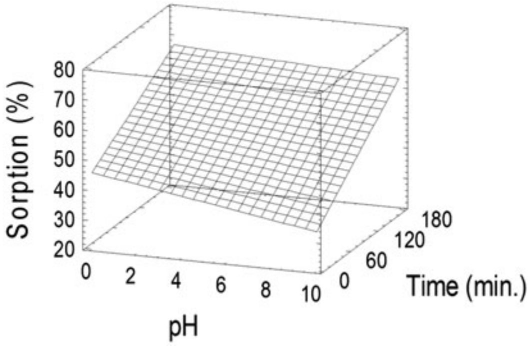

Fig. 5(b). Response surface plots for interaction effect of time and pH on removal.

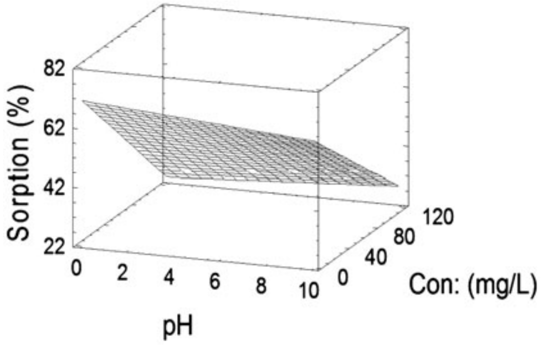

Fig. 5(c). Response surface plots for interaction effect of pH and time on removal.

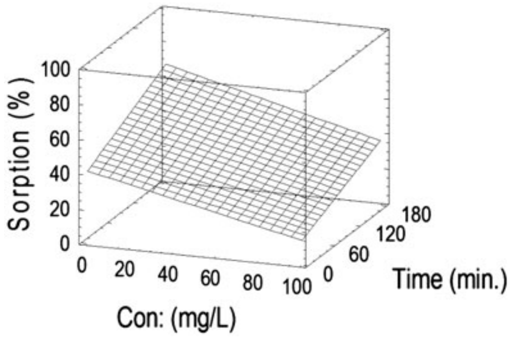

Fig. 5(d). Response surface plots for interaction effect of concentration of arsenic solution and time on removal.

Table 3
Analysis of variance for model tested for the removal of arsenic

Term	*F*-ratio	*p*-value
A: Amount	0.1	0.3931
B: PH	45.1	0.0067
C: Concentration	832.4	0.0001
D: Time	618.6	0.0001
AB	30.5	0.0117
AC	391.1	0.0003
AD	179.9	0.0009
BC	30.5	0.0117
BD	30.5	0.0117
CD	2.5	0.2124

concentration (832.4) > time (618.6) > pH (45.1) > amount (0.1). The p values are smaller than 0.05, which shows that the model is statistically significant [21]. The highest value of F is for concentration with the lowest value of p (0.001), which shows that the term concentration is highly significant for the removal of arsenic from aqueous systems.

3.7. Predicted optimum parameters and method validation

Optimum predicted values of amount, concentration, pH, and time obtained for arsenic removal were; amount 57 mg, concentration 10 mg L^{-1}, pH 5.5, and time 160 min. Optimum sorption conditions determined from mathematical model were validated by conducting sorption experiment at optimum predicted conditions. A good agreement between the experimental values (98.9%) and the predicted values (100%) for the removal of arsenic were found. These values show the successful application of CCD model for prediction of optimum parameters for the removal of arsenic.

4. Sorption isotherms

In order to design the adsorption system, it is very important to examine the equilibrium adsorption isotherms. Several isotherms are available for solid–liquid systems, the Langmuir isotherm (Eq. (2)) is based on the assumption that the adsorption occurs at specific homogeneous sites within the adsorbent, whereas the Freundlich isotherm (Eq. (3)) is an empirical equation employed to describe the heterogeneous system.

$$\frac{C_e}{C_{ads}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{2}$$

$$\log C_{ads} = \log\ K_F + \frac{1}{n_F}\log C_e \tag{3}$$

The Dubinin–Radushkevitch (D–R) equation (Eq. (4)), is an empirical adaptation of Polanyi adsorption potential theory, is the fundamental equation to quantitatively describe the adsorption by microporous sorbents.

$$\ln \text{Cads} = \text{KD} - \text{R} - \beta\varepsilon^2 \tag{4}$$

where Cads is the amount of metal ions adsorbed per unit mass of modified Amberlite XAD-2 resin and C_e is the amount of arsenic ions in liquid phase at equilibrium, Q, b, K, $1/n$, and β are the, Freundlich, Langmuir, and D–R constants, respectively [22]. All three isotherm equations (Eqs. (2)–(4)) were found to be linear with co-efficient of co-relation values (r) equal to 0.986, 0.978, and 0.997, respectively, for Langmuir, Freundlich and D–R adsorption isotherm. Values of sorption capacities calculated from intercept/slope of curves were 227μmol g^{-1}, 85.9 mmol g^{-}1, and 125 μmol g^{-1}, respectively.

Langmuir adsorption isotherm can also be explained in terms of separation factor which can be calculated by using Eq. (5):

$$R_L = 1/(1 + bC_i) \tag{5}$$

R_L describes the type of Langmuir isotherm [23] to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), or unfavorable ($R_L > 1$). R_L factor calculated for the sorption of arsenic on modified resin was found to be in the range of 0.13–0.78 indicating the favorable sorption. The values of energy of adsorption (E) calculated from the slope (β) of the D–R plot using Eq. (6) was 12 kJ mol^{-1}, which is in the range of 9–16 kJ mol^{-1} and is expected for chemisorption or ion exchange nature of sorption [24].

$$E = 1/\sqrt{} - 2\beta \tag{6}$$

5. Kinetics of sorption

The kinetics of sorption of arsenic on modified XAD-2 was evaluated by varying the agitation time and keeping other parameters i.e. pH, concentration, and amount at their optimum values, obtained data was subjected to the linear form of Lagergren's first-order rate equation [25] (Eq. (7)) and Moris-Weber (Eq. (8)) equation.

$$\ln(q_e - q_t) = \ln q_e - K_t \tag{7}$$

The Lagergren's plot was found to be linear with correlation coefficient of 0.987, the calculated value of q_e (0.12 mmol g^{-1}) was also in agreement with the experimental q_e value (0.18 mmol g^{-1}) indicating that Lagergren's equation is appropriate to explain arsenic uptake by modified XAD-2. The value of first-order rate constant found from the slope of the linear curve was 0.0071 min^{-1}.

Mechanisms and rate controlling steps affecting the kinetics of adsorption was assessed by fitting adsorption data to the Weber's intraparticle diffusion model.

$$q_t = k_{\text{ird}}\sqrt{t} + C \tag{8}$$

where k_{ird} is the intraparticle diffusion rate constant (μmol g^{-1} min$^{-1/2}$), which can be evaluated from the slope of the linear plot of q_t vs. $t^{1/2}$ as shown in Fig. 6. The intercept of the plot reflects the boundary layer effect. As the regression of q_t vs. $t^{1/2}$ does not pass through the origin, it can be concluded that the intraparticle diffusion is not the sole rate-limiting step [26].

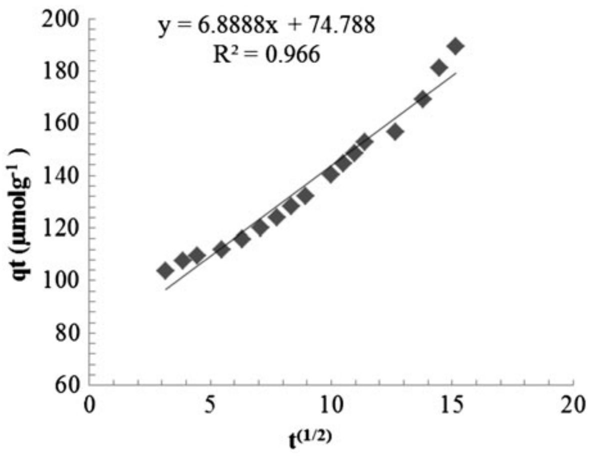

Fig. 6. Morris–Weber plot for the removal of arsenic by modified XAD-2.

Table 4
Removal of arsenic from real water samples

	Arsenic conc. in sample ($\mu g\ L^{-1}$)			
Samples	Actual	Added	% Recovery	Residual amount ($\mu g\ L^{-1}$)
1	11.58	–	88.90	1.28
	11.58	25	90.5	3.47
2	0.55	–	91.0	0.049
	0.55	25	93.4	1.68

Table 5
Comparison of adsorption capacities ($mg\ g^{-1}$) of different adsorbents based on Langmuir model

Adsorbent	Arsenic sorption capacity ($mg\ g^{-1}$)	Reference
Iron oxide-coated sand IOCS	0.018	[27]
Iron oxide-coated sand	0.043	[28]
Iron oxide-coated sand IOCS-2	0.008	[29]
Activated Bauxsol (AB)	7.642	[30,31]
Re mud (RRM)	0.514	[32]
Polymetallic sea nodule	2.830	[33]
ZMA (Sonora)	0.100	[34,35]
Fe(III) oxide-impregnated GAC	4.500	[36]
Fe-hydrotalcite-supported magnetite nanoparticle	1.280	[37]
Zerovalent iron-impregnated chitosan-caboxymethyl-bcyclodextrin composite beads	13.51	[38]
Nanoscale zero valent iron-reduced graphite oxide modified composites	29.04	[39]
Fe-Schiff's base-modified XAD-2	17.02	Present work

6. Treatment of arsenic-contaminated water

After optimization of factors effecting the removal, this method was tested for its effectiveness to treat the arsenic-contaminated water samples. Sample (S1) was taken at the draining point in Karachi Wah, Jamshoro, Pakistan. Sample (S2) was taken from tube well water, Pakistan. Table 4 shows the removal of up to 93%, whereas the residual concentration of arsenic in drinking water after removal is less than that of the WHO recommended maximum contaminant level i.e. 10 $\mu g\ L^{-1}$. These results show the effectiveness of resin for the treatment of arsenic-contaminated water.

7. Comparison with reported methods

Table 5 compares the adsorption capacity values calculated for the removal of arsenic using iron-based as well as other adsorbent materials with modified XAD-2 [27–39]. Adsorption capacity of iron-Schiff's base-modified XAD-2 is comparable with most of the adsorbents, whereas its preparation is relatively simple.

8. Conclusion

In the present study, a very simple and effective method for the treatment of arsenic-contaminated water systems is developed. Schiff base, bis-acetylacetone ethylenediimine and its iron complex can be prepared easily by simple synthesis procedure. Impregnation of Schiff base onto XAD-2 was found to be very stable and complex did not leach from the surface during sorption experiments. Results showed the successful application of Drape–Lin composite design with correlation values of $R^2 = 99.98\%$ and $R^2_{adj.} = 99.92\%$ for prediction of optimum sorption parameters effecting the removal of arsenic by modified resin. Residual concentrations in arsenic-contaminated water samples were well in safe limit set by WHO, showing the effectiveness of developed method.

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