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Studies on removal of phenol using ionic liquid immobilized polymeric micro-capsules

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Micro-encapsulation;
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Abstract Phenol and phenolic compounds are pollutants of high priority concerns because of their toxicity and contribution to health problems. (Lohumi et al., 2004) The most suitable industrial process for the removal of phenol from aqueous streams is liquid–liquid extraction, which has its own limitations. In order to avoid possible drawbacks, such as persistent emulsification and leaching of extractant in conventional extraction operations, room temperature ionic liquid (RTIL) encapsulated in microcapsules (MC) is used as extractant.

The present study deals with the preparation of RTIL encapsulated microspheres by surfactant free emulsion polymerization under controlled conditions and the microspheres thus synthesized are characterized to ensure the desired particle size, morphology and surface area by using Scanning Electron Microscopy (SEM), FTIR and BET apparatus, respectively.

The effects of process variables such as agitation speed, agitation time, temperature, and shell material and the effect of dispersant were studied to determine the yield and size of microcapsules. This was followed by equilibrium distribution studies. The extractant loading capacity in the microcapsules was also analyzed by solvent extraction using hexane as solvent. Batch Sorption studies were conducted to optimize the process variables in the removal of phenol and the data were validated using various isotherms and kinetic models. Thermodynamic parameters were also established. Regeneration studies were also attempted to ensure the stability and reusability of microcapsules.

1. Introduction

Phenol and its derivatives, as one of the most important organic intermediates, have been widely used for the manufacture of pesticides, rubber, drugs and dyestuffs. As a result, more and more phenol-containing wastewater has been discharged into water bodies. Phenolic compounds are pollutants of high priority concerns because of their toxicity and contribution to health problems (Lohumi et al., 2004; Ram et al., 1990; He and Huang, 1992). Various methods of wastewater treatment, such as cata-

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lytic oxidation, liquid membrane separation, biological degradation and adsorption have been developed (Orshansky and Narkis, 1997; Deiber et al., 1997). Due to the ability of typical adsorbents to adsorb even at high concentrations, the adsorption process has been proved to be one of the most attractive and effective techniques for the separation of pollutants and purification in wastewater treatment (Wang et al., 2004; Fei et al., 2004; Zhai et al., 2003; Cai et al., 2005a, b; Wang, 2004).

In recent years, the polymeric microcapsules (MCs) have been extensively used for the recovery of metal ion pollutants (Araneda et al., 2008) and for drug delivery (Singh et al., 2010; Venkatesan et al., 2009). The MCs correspond to a porous polymeric matrix that contains an encapsulated suitable extracting reagent, room temperature ionic liquids (RTIL), called extractant which is chosen to selectively extract the desired pollutants. RTILs are organic or organo-elemental salts which exist as liquids at room temperature and they perform as ''green solvents'' due to their negligible volatility, high thermal stability, high electrical conductivity, low nucleophilicity and eco friendliness. The potential advantages of MCs are easy phase separation, large specific interfacial area, minimal use of organic solvent, high selectivity and more stability of extractant.

Optimization of the process variables is needed to achieve the maximum adsorption capacity and removal efficiency. The conventional method of optimizing the process variables requires a very large number of experimental runs which is highly expensive and time consuming. This limitation can be overcome by the statistical design of experiments, which reduces the number of experiments and provides an appropriate model for process optimization. Response surface modeling (RSM) is a useful method to optimize the responses shaped under the influence of process variables (Wang and Fei, 2006; Singh et al., 2011; Wan Ngah et al., 2008; Tao et al., 2009; Jain and Kadirvelu, 2011; Kincl et al., 2005; Singh et al., 2011; Tanyildizi, 2011; Ahmad and Ahmad, 2009; Sahu and Meikap, 2009; Kalavathy et al., 2009; Mohammed and Ahmad, 2010).

The present work deals with the preparation and characterization of RTIL encapsulated MCs under controlled conditions to evaluate the effect of process variables and dispersant in the synthesis of MCs with respect to their yield, size and shell material. The synthesized RTIL encapsulated MCs were used for the removal of phenol from aqueous solution. RSM was used to optimize the process parameters affecting the adsorption such as initial concentration of feed solution, adsorbent dosage, pH of feed solution and temperature.

2. Methodology

2.1. Materials

Gum arabic from acacia tree (Sigma) and Gelatin from porcine skin (Fluka) were used as dispersants for the preparation of microcapsules. Styrene (Alfa Aesar), Divinyl benzene (Alfa Aesar) and ethylene glycol dimethacrylate (Alfa Aesar) were used as monomers. Trioctylphosphineoxide 90% (Cyanex – 923) was the room temperature ionic liquid used as extractant. Benzoyl peroxide (Fluka), as polymerization initiator and toluene as diluent were also used. Phenol, 4-aminoantipyrene, Potassium ferricyanide, Phosphate buffer, 0.5 N ammonium solution, 0.1 N HCl solution, 0.1 M NaOH solution and deionized water were the other chemicals used.

2.2. Preparation of adsorbent

The synthesis of RTIL encapsulated polymer microcapsules was carried out in a batch reactor of 1.0 L capacity. A mixture of 250 mL de-ionized water and 1% of dispersant by weight as continuous phase was placed in the reactor and stirred continuously at a desired agitation speed under inert atmosphere. The organic solutions of styrene and divinylbenzene (1:1 weight ratio), Benzoyl peroxide and RTIL with diluent were used as the dispersed phase. The dispersed phase was added when the temperature of the continuous phase reached the specified temperature and prolonged for 4 h to reach a high conversion of monomers to Polymer MCs. The resulting microcapsules were filtered, repeatedly washed with de-ionized water and then dried at room temperature.

2.3. Characterization of RTIL encapsulated MCs

Synthesized MCs were characterized to determine the specific surface area of the MCs using a surface area analyzer (GeminiV2.00 Micromeritics). The morphological structure and particle size were observed using Scanning Electron Microscopy (Hitachi S3000H). FTIR spectra were recorded using FTIR spectrophotometer (Perkin Elmer, spectrum RXI) to analyze the presence of RTIL within the polymer core shell.

2.4. Adsorption experiments

Batch adsorption studies were conducted to determine the adsorption capacity and percentage removal of phenol using RTIL encapsulated MCs. A specific quantity of RTIL encapsulated MCs was brought in contact with 50 mL of phenol solution of known concentration at a particular pH and agitated in a rotary shaker at 200 rpm. The experiments were carried out by varying MC dosage, initial phenol concentration, contact time, temperature and pH. The samples were withdrawn at predetermined time intervals and analyzed for their phenol content spectrophotometrically at 500 nm using a UV spectrophotometer (JASCO UV Spectrophotometer). The amount of adsorption at equilibrium, q_e (mg/g), and percentage removal (percentage) were calculated using Eq. (1) and Eq. (2).

$$q_e = (C_0 - C_e)V/m \quad (1)$$

$$\text{Percentage removal} = [(C_0 - C_e)/C_0] \times 100 \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations (mg/l), m is the weight of adsorbent (g), q_e is the adsorbed quantity or adsorption capacity (mg/g) and V is the volume of solution.

2.5. Regeneration studies

Phenol loaded RTIL encapsulated MCs were regenerated to check the reactivity and stability of extractant. NaOH and $Ba(OH)_2$ were reported (Ozakya, 2006; Rinkus et al., 1997) as the most efficient stripping solutions for Phenol. Desorption studies were carried out by using 50 ml of 0.1 N NaOH solution with the spent adsorbent at a pH of 11 and agitated for 2 h at 200 rpm. After desorption of phenol, the RTIL encapsulated MCs were washed with distilled water until they are neu-

tralized and then desiccated at room temperature. The sorption process was repeated by using the regenerated RTIL encapsulated MCs.

2.6. Response surface modeling

RSM is a statistical method based on the multivariate non-linear model that has been widely used for the optimization of adsorption process variables and also used to determine the regression model equations and operating conditions from the appropriate experiments. It is also useful in studying the interactions of the various parameters that affect the process.

The standard RSM design called Central Composite design (CCD) was applied in this present study to determine the optimum process variables for adsorption of phenol using RTIL encapsulated MCs. The CCD was used for fitting a second order model which requires only a minimum number of experiments for modeling (Tanyildizi, 2011; Ahmad and Ahmad, 2009; Sahu and Meikap, 2009; Kalavathy et al., 2009; Mohammed and Ahmad, 2010). The CCD consists of 2^n factorial runs (coded to the usual ± notation) with $2n$ axial runs ($\pm\alpha$,0,0,0), (0, $\pm\alpha$,0,0 . . .,0), . . . (0,0, . . . , $\pm\alpha$) and n_c center runs (six replicates,0,0,0 . . . 0). The number of factors n increases the number of runs for a complete replicate of the design which is given in Eq. (3). (Kalavathy et al., 2009; Mohammed and Ahmad, 2010).

$$N = 2^n + 2n + n_c \tag{3}$$

An empirical model was developed to correlate the response to the adsorption of Phenol from aqueous solution using RTIL encapsulated MCs based on second order as given by Eq. (4).

$$Y = b_0' + \sum_{i=1}^{n} b_i X_i + \sum_{i=1}^{n} b_{ii} X_i^2 + \sum_{i=1}^{n} \sum_{j>1}^{n} b_{ij} X_i X_j \tag{4}$$

where Y is the predicted response, b_0' is the constant coefficient, b_i is the linear coefficient, b_{ij} is the interaction coefficient, b_{ii} is the quadratic coefficient and X_i, X_j are the coded values.

3. Results and discussion

The results obtained from the present investigation on the synthesis of MCs and their application for the removal of Phenol are discussed below in detail.

3.1. Preparation and characterization of MCs

In this present study, experiments were conducted to determine the effect of shell material and that of dispersant on the preparation of RTIL encapsulated microcapsules for optimizing the process variables.

3.1.1. Effect of temperature

Microcapsules were prepared by using Styrene-Divinyl benzene (St-DVB) as shell materials, arabic gum as dispersant and cyanex-923 as RTIL solvent. The experiments were carried out by varying temperatures 60–70 °C at 600 rpm for 3 h. The results obtained confirm that the polymerization reaction is highly influenced by the temperature.

It was observed that at 60 °C and 65 °C, only an oily layer was observed without any precipitate. At 70 °C microcapsules of size 10–300 μm were formed and the yield was found to be

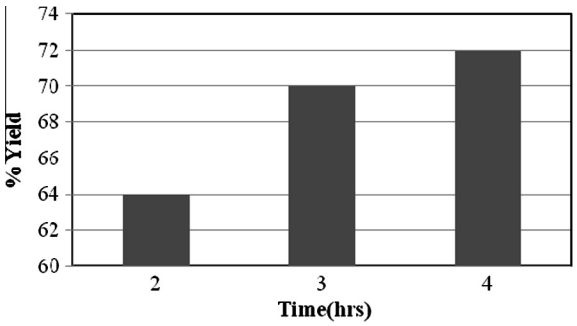

Figure 1 Effect of time on %yield of MCs.

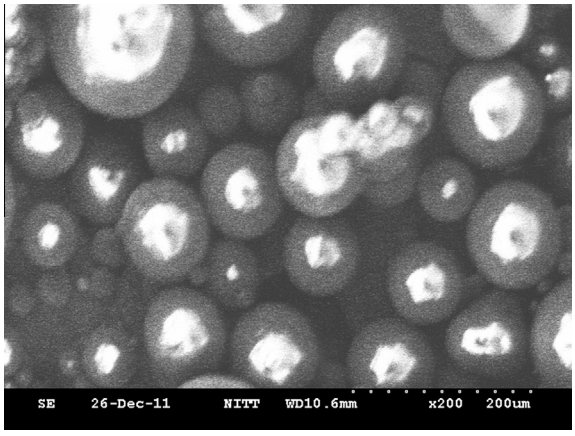

Figure 2 SEM image of blank microcapsules.

70%. Above 70 °C rapid loss of continuous phase was observed. Hence, the temperature is optimized as 70 °C for obtaining microcapsules.

3.1.2. Effect of time

The experiments were conducted for various time durations of 2–4 h, at 600 rpm and 70 °C in order to optimize the time duration of polymerization reaction and it is found that the yields are 64%, 70% and 72%, respectively as shown in Fig. 1.

Fig. 2 shows the image of blank MCs without RTIL while, Figs. 3–5 represent the RTIL encapsulated MCs at different times of the reaction. From these figures, the size of the microcapsules observed was 2–100 μm for 2 h of reaction and the same was found to be in the range of 10–300 μm for 3 h and 4 h of reaction time. Since the yield is more along with a favorable size of the particles and with less aggregation (that is discrete particle) the time duration for the polymerization reaction is optimized as 4 h. The surface area of the MCs obtained at 4 h of reaction time was measured by BET analyzer and it was found to be 5.949 m^2/g.

3.1.3. Effect of speed

Experiments were carried out at different speeds at 500 rpm, 600 rpm and 700 rpm at a constant temperature of 70 °C and a reaction time of 4 h in order to optimize the speed of agitation. The yield of MCs and the particle size obtained at 500 rpm, 600 rpm and 700 rpm are given in Table 1. It indicates that particles in micron size are formed only at 600 rpm. Hence, the speed of agitation is optimized as 600 rpm.

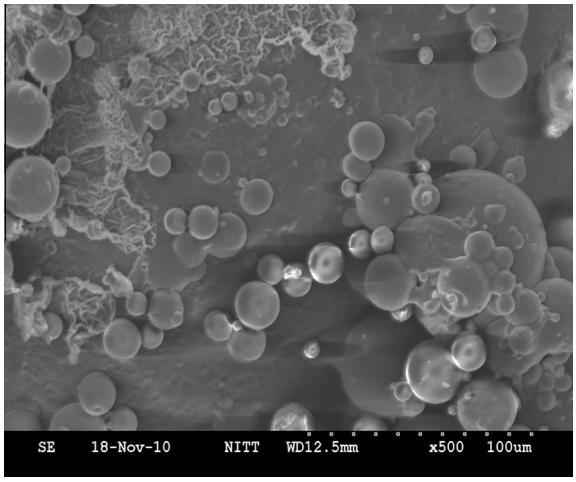

Figure 3 SEM image of microcapsules for 2 h of reaction.

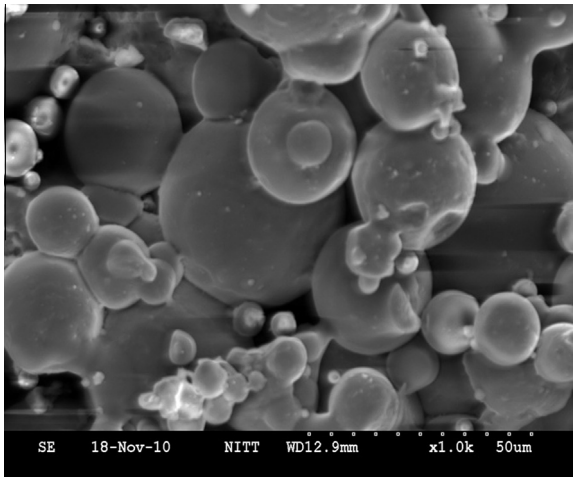

Figure 4 SEM image of microcapsules for 3 h of reaction.

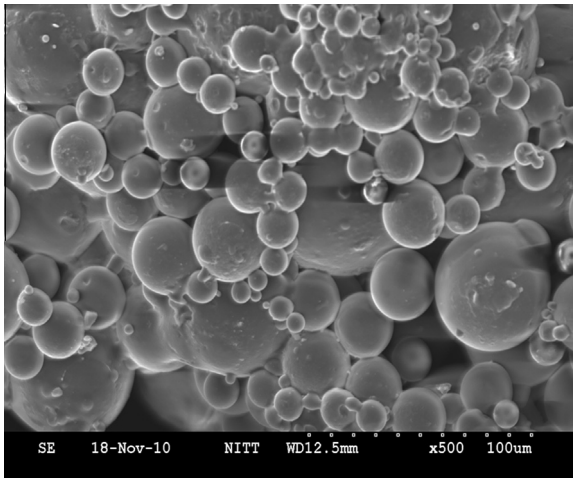

Figure 5 SEM image of microcapsules for 4 h of reaction.

Table 1 Percentage yield and size range of particles at various speeds.

Speed(rpm)	%yield	Size
500	73	0.5–1 mm
600	72	10–300 μm
700	66	2–4 mm

At a higher speed of 700, probably due to agglomeration of particles, the observed size of particles is higher.

3.1.4. FT-IR analysis of encapsulated microcapsules

FTIR is the most powerful tool for identifying the type of functional groups in a sample.

This study will help in confirming the presence of RTIL in microcapsules. The FTIR spectrum of encapsulated microcapsules is shown in Fig. 6. Band observed at 1629.13 cm^{-1} was due to the presence of C═C in ring. Band at 3187.90 cm^{-1} was due to the presence of alkene ═C–H and ═CH_2. Band observed at 704.63 cm^{-1} indicated the presence of aromatic C–H bond. Peak at 1265.31 cm^{-1} was attributed to the vibration of P═O phosphonate group. The presence of P═O bond indicates the presence of cyanex-923, the ionic liquid, in the present study.

3.1.5. Effect of shell material on microcapsule preparation

The effect of shell material on the formation of MCs was carried out by comparing the MCs of St-DVB with MCs of St-EGDMA under optimized conditions. The percentage yield of St-EGDMA MCs obtained was found to be 91%. The SEM image of MCs is shown in Fig. 7.

The SEM image revealed an irregular shape and structure of the microcapsules. Also, the particle was found to be bigger in size and aggregation was also more. The size of St-EGDMA MCs was estimated to be in the range of 300–1000 μm. If the particle size is bigger, then the interfacial area will be less which will result in reduction of rate of diffusion.

3.1.6. Effect of dispersant on microcapsule preparation

The effect of dispersant on the preparation of MCs was analyzed by using gelatin instead of arabic gum as dispersant, St-DVB as monomers and cyanex-923 as solvent under optimum conditions estimated earlier. The SEM image as shown in Fig. 8 indicated that MCs spherical in shape were formed. However, gelatin changed the surface nature of the microcapsules indicating a porous morphology compared to the particles formed while using arabic gum as dispersant. The size of the particles was found to be in the range of 100–300 μm. The yield of MCs obtained was found to be only 46% when gelatin was used as dispersant.

3.1.7. Extractant loading capacity

Extractant loading ratio was found by the solvent extraction method using heptane as solvent. RTIL loading capacity for St-DVB with arabic gum, St-DVB with gelatin and St-EDGMA with arabic gum was found to be 43.6%, 46.5% and 36.4%, respectively.

Hence, it was decided to use St-DVB MCs with arabic gum as dispersant and Cyanex 923 as extractant in the present study.

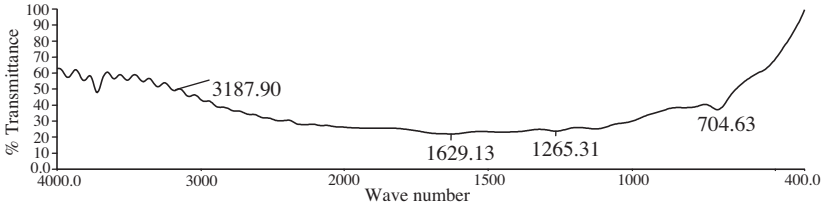

Figure 6 FT-IR spectrum of encapsulated microcapsules.

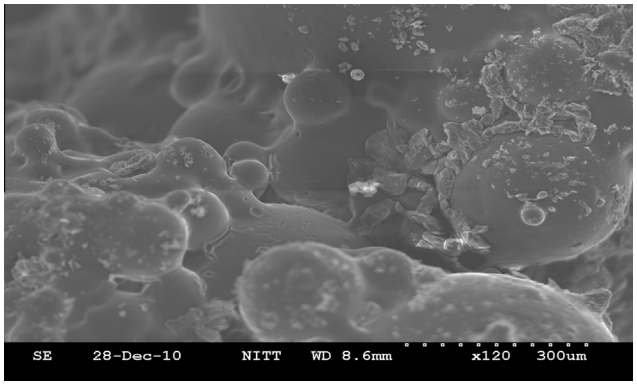

Figure 7 SEM image of RTIL encapsulated St-EGDMA MCs.

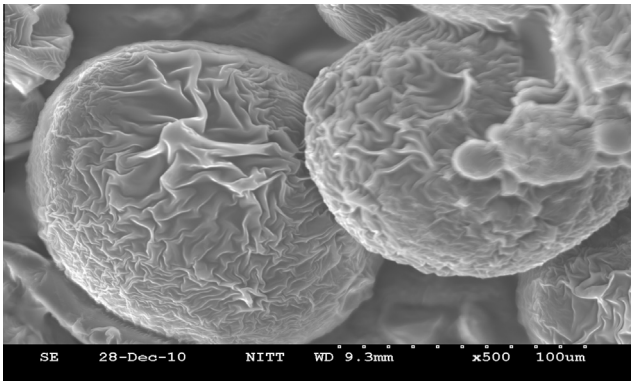

Figure 8 SEM image of St-DVB MCs with gelatin as dispersant.

3.2. Sorption studies

MCs synthesized were used to determine the removal efficiency of phenol from aqueous solutions.

3.2.1. Effect of agitation speed

The effect of agitation speed on adsorption capacity of phenol was studied using RTIL encapsulated MCs for various agitation speeds at an initial concentration of 50 ppm, dosage of 0.5 g MCs and a pH of 6.0. The results obtained indicate that the adsorption capacity varied insignificantly between 200 and 300 rpm. Hence, the agitation speed was chosen as 200 rpm for further sorption studies.

3.2.2. Effect of contact time and concentration

The effect of contact time on adsorption capacity of phenol using RTIL encapsulated MCs at a constant pH of 6.0, dosage

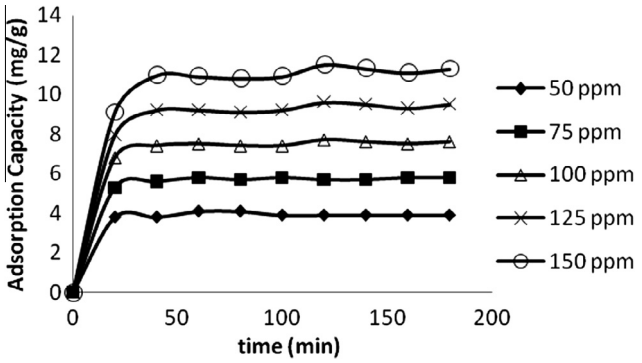

Figure 9 Effect of contact time and initial concentrations on adsorption capacity of RTIL encapsulated MCs.

of 0.5 g MCs, agitation speed of 200 rpm and at a temperature of 30 °C for various initial concentrations of the solution is presented in Fig. 9. From the results, it was observed that the equilibrium time required for the adsorption of phenol on MCs was almost 90 min. The results also indicated that up to 70–80% of the total amount of phenol uptake was found to occur in the first rapid phase (40 min) and thereafter the sorption rate was found to be constant. The higher sorption rate at the initial period was due to the availability of the increased number of vacant sites on the adsorbent and as a result of this increased concentration gradients developed between adsorbate in solution and adsorbate on the adsorbent surface (Uddin et al., 2007). A similar trend was observed at all concentrations of solutions. It was also observed that an increase in initial concentration resulted in an increased phenol uptake due to increased driving force for the mass transfer.

3.2.3. Effect of pH

The effect of pH on adsorption capacity and percentage removal of phenol using RTIL encapsulated MCs at a dosage of 0.5 g MCs, agitation speed of 200 rpm, at a temperature of 30 °C for an initial concentration of 100 ppm is presented in Fig. 10(a) and (b) respectively.

3.3. Regeneration and reusability of RTIL encapsulated MCs

The regeneration experiments were carried out to test the feasibility of chemical regeneration of the MCs-Cyanex923 loaded with phenol. Fig. 11 shows the effect of repeatability cycles on percentage removal. It was found that for the first 2 cycles, the percentage removal is more or less the same. However, in the 3rd cycle there is a drop in the percentage removal of phenol under identical conditions. Hence, it may be taken that the

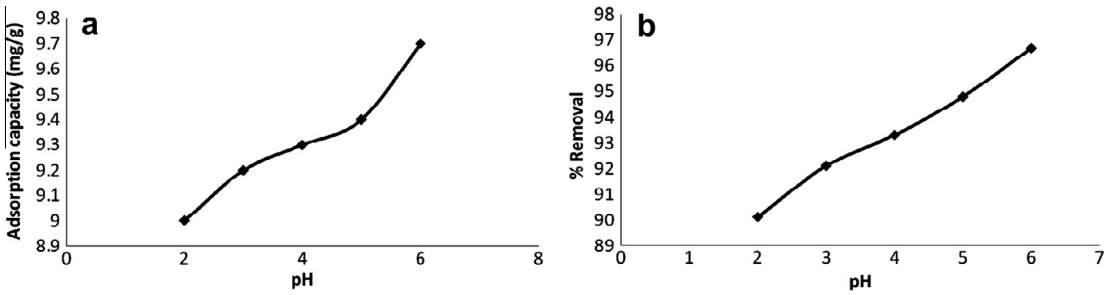

Figure 10 (a) and (b) Effect of pH on adsorption capacity of RTIL encapsulated MCs.

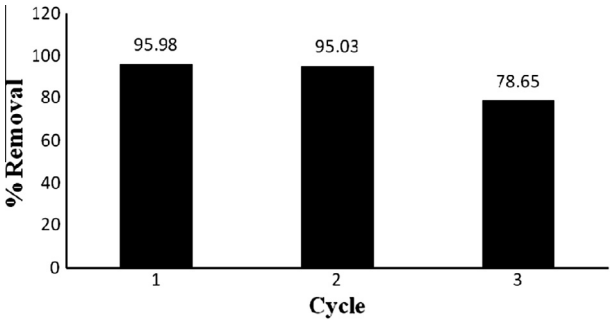

Figure 11 The effect of percentage removal on phenol using regenerated RTIL encapsulated MCs.

MCs can be used up to 3 cycles. The result also shows the stability of the extractant in the microcapsules.

3.4. Development of regression model equation using CCD

In this present investigation, for CCD three variables such as adsorbent dosage (g), pH and initial concentration (mg/l) each with five levels (± 1 for the factorial points, 0 for the center points and $\pm\ \alpha$ for the axial points) were chosen as independent variables with the designated coded factors as A, B, and C, respectively and the variables are given in Table 2.

A total of 20 experiments were necessary to estimate the coefficients of each model using linear regression analysis. The two dependent output responses viz., percentage removal (Y_1) and adsorption capacity (mg/g) (Y_2) were obtained from the independent input variables for CCD and are presented in Table 3 as response 1 and 2, respectively.

The quadratic model was suggested by the Design expert software version 8 for percentage removal (Y_1) and adsorption capacity (Y_2) of phenol removal using RTIL encapsulated MCs adsorbent. The higher order polynomials obtained are given in Eqs. (5) and (6). The Model summary statistics for percentage removal of phenol and adsorption capacity of phenol using RTIL encapsulated MCs is presented in Tables 4 and 5 respectively

Table 3 Experimental design matrix and responses for the adsorption of phenol using RTIL encapsulated MCs.

Run	Factor 1	Factor 2	Factor 3	Response 1	Response 2
	A	*B*	*C*	Y_1	Y_2
1	3	0.2	75	62.5	11.7
2	5	0.2	75	65.6	12.3
3	3	0.4	75	84.9	7.95
4	5	0.4	75	87.9	8.2
5	3	0.2	125	58.0	18.1
6	5	0.2	125	61.0	19.1
7	3	0.4	125	80.4	12.6
8	5	0.4	125	83.4	13.0
9	2	0.3	100	74.2	12.4
10	6	0.3	100	80.8	13.5
11	4	0.1	100	36.5	18.3
12	4	0.5	100	93.3	9.3
13	4	0.3	50	81.9	6.8
14	4	0.3	150	73.4	18.4
15	4	0.3	100	77.4	12.9
16	4	0.3	100	77.4	12.9
17	4	0.3	100	77.4	12.9
18	4	0.3	100	77.4	12.9
19	4	0.3	100	77.4	12.9
20	4	0.3	100	77.4	12.9

The quadratic model obtained for the percentage removal (Y_1) and adsorption capacity (Y_2) of phenol using RTIL encapsulated MCs adsorbent in terms of coded factors is reported as Eq. (5) and Eq. (6)

$$Y_1 = 77.15 + 1.58A + 12.69B - 2.19C - 0.01AB - 0.012AC + 0.013BC - 0.10A^2 - 3.25B^2 - 0.065C^2 \quad (5)$$

$$Y_2 = 12.87 + 0.27A - 2..35B + 2.87C - 0.11AB + 0.056AC - 0.48BC - 3.977E^{-003}A^2 + 0.21B^2 - 0.091C^2 \quad (6)$$

The R^2 for Eq. (5) and (6) were found to be 0.9851and 0.9986, respectively. These values are close to unity and lead to

Table 2 Variables and levels considered for the adsorption of phenol using RTIL encapsulated MCs by CCD.

Variables	Levels						
	Units	Symbol	$-\alpha$	-1	0	$+1$	$+\alpha$
pH	–	A	2	3	4	5	6
Dosage	Gram	B	0.1	0.2	0.3	0.4	0.5
Initial concentration	ppm	C	50	75	100	125	150

Table 4 Model summary statistics for percentage removal of phenol using RTIL encapsulated Mcs.

Source	Standard deviation	R^2	Adj R^2	Predicted R^2	Press	Comments
Linear	4.53	0.8916	0.8712	0.7989	607.78	
2F1	5.02	0.8916	0.8415	0.7418	780.61	
Quadratic	2.12	0.9851	0.9717	0.8766	373.10	Suggested
Cubic	1.19	0.9972	0.9910	0.4189	1756.10	Aliased

Table 5 Model summary statistics for adsorption capacity of phenol using RTIL encapsulated MCs.

Source	Standard deviation	R^2	Adj R^2	Predicted R^2	Press	Comments
Linear	0.49	0.9828	0.9796	0.9679	7.22	
2F1	0.38	0.9915	0.9876	0.9801	4.48	
Quadratic	0.18	0.9986	0.9974	0.9888	2.57	Suggested
Cubic	0.15	0.9994	0.9980	0.8692	29.14	Aliased

Table 6 Analysis of variance (ANOVA) for response surface quadratic model for percentage removal of phenol using RTIL encapsulated MCs.

Source	Sum of squares	DF	Mean square	F value	P value	
Model	2977.93	9	330.88	73.52	<0.0001	Significant
A	40.01	1	40.01	8.89	0.0138	
B	2578.10	1	2578.10	572.84	<0.0001	
C	77	1	77	17.11	0.0020	
AB	1.250 E^{-003}	1	1.250 E^{-003}	2.777E^{-004}	0.9870	
AC	1.250 E^{-003}	1	1.250 E^{-003}	2.777E^{-004}	0.9870	
BC	1.250 E^{-003}	1	1.250 E^{-003}	2.777E^{-004}	0.9870	
A^2	0.26	1	0.26	0.058	0.8139	
B^2	265.94	1	265.94	59.09	<0.0001	
C^2	0.11	1	0.11	0.023	0.8814	
Residual	45.01	10	4.5			
Lack of fit	45.01	5	9.0			
Pure error	0.000	5	0.000			
Cor total	3022.94	19				

Table 7 Analysis of variance (ANOVA) for response surface quadratic model for adsorption capacity of phenol using RTIL encapsulated MCs.

Source	Sum of squares	DF	Mean square	F value	P value	
Model	224.84	9	24.98	808.13	<0.0001	Significant
A	1.18	1	1.18	38.26	0.0001	
B	88.13	1	88.13	2850.71	<0.0001	
C	131.96	1	131.96	4268.79	<0.0001	
AB	0.090	1	0.090	2.92	0.1182	
AC	0.025	1	0.025	0.82	0.3868	
BC	1.85	1	1.85	59.94	<0.0001	
A^2	3.977E-004	1	3.977E-004	0.013	0.9119	
B^2	1.09	1	1.09	35.37	0.0001	
C^2	0.21	1	0.21	6.81	0.0261	
Residual	0.31	10	0.031			
Lack of fit	0.31	5	0.062			
Pure error	0.000	5	0.000			
Cor total	225.15	19				

prediction of percentage removal and adsorption capacity close to experimental values.

The analysis of variance from Eq. (5) and Eq. (6) is reported in Tables 6 and 7. The model F-value of 73.52 and Prob > F less than 0.05 implies that the model is significant for percentage removal. The model F-value of 808.13 and Prob > F less than 0.05 implies that the model was significant for adsorption capacity. Values of "Prob > F" less than 0.05,

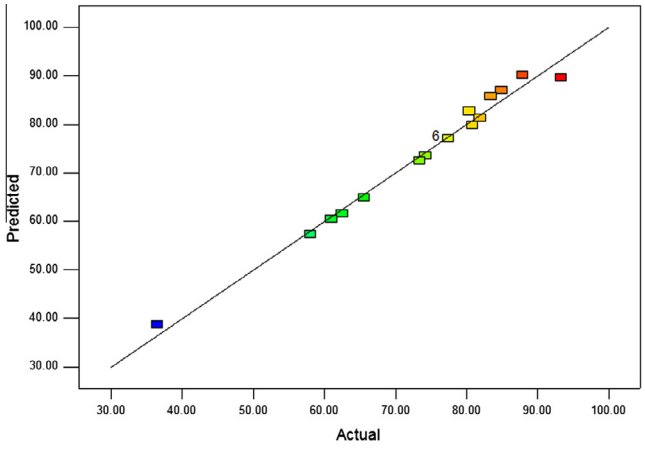

Figure 12 The actual and predicted plot for percentage removal of phenol using RTIL encapsulated MCs.

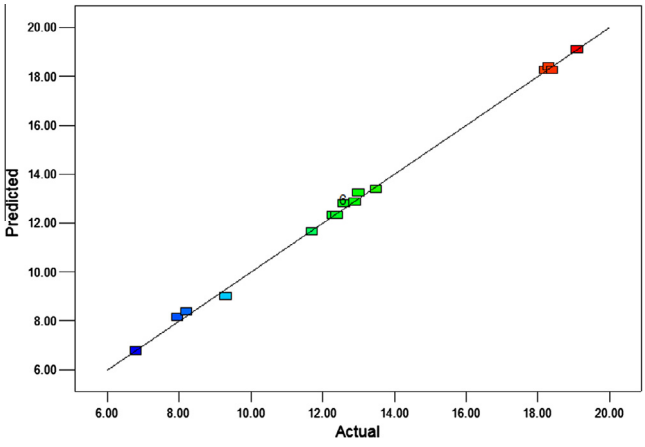

Figure 13 The actual and predicted plot for adsorption capacity of phenol using RTIL encapsulated MCs.

indicate model terms are significant and values greater than 0.1000 indicate that the model terms are not significant. For percentage removal, the terms A, B, C and B^2 were significant model terms and for adsorption capacity, the terms A, B, C, BC, B^2 and C^2 were significant model terms.

Based on the statistical results it has been found that the model is adequate to predict the percentage removal and adsorption capacity in the range of variables studied. Figs. 12 and 13 show the predicted values versus the experimental values for percentage removal and adsorption capacity, respectively. It can be seen that the response models show good fits to the experimental data and hence reflected good predictions from the models.

3.5. Interaction effects of process variables

The interactive effect of process variables on percentage removal and adsorption capacity of phenol using RTIL encapsulated MCs is represented through three dimensional surface response plots and is shown in Figs. 14–16

3.5.1. The combined effect of pH and adsorbent dosage

The combined effect of pH and adsorbent dosage on percentage removal and adsorption capacity of phenol using RTIL encapsulated MCs is shown in Figs. 14(a) and (b) respectively. Highest adsorption capacity and percentage removal were observed at a pH of 6. Phenol exists in molecular form in the range of pH $\leqslant$7. After that, its anionic fraction increases with an increase in aqueous phase pH. Hydrogen-bonding and hydrophobic interactions between ionic liquids and the phenols make it easy for the transfer of phenols from aqueous solutions to the ionic liquid phases, leading to high distribution ratios observed experimentally. The maximum percentage removal of 88% and an adsorption capacity of 10.9 mg/g were obtained at an adsorbent dosage of 0.4 g and at a pH of 6 for a constant initial concentration of 100 ppm.

3.5.2. The combined effect of initial metal ion concentration and adsorbent dosage

The combined effect of adsorbent dosage and initial concentration on percentage removal and adsorption capacity of phenol using RTIL encapsulated MCs is shown in Figs. 15(a) and (b) respectively. The adsorption capacity decreased with an increased adsorbent dosage whereas the percentage removal of

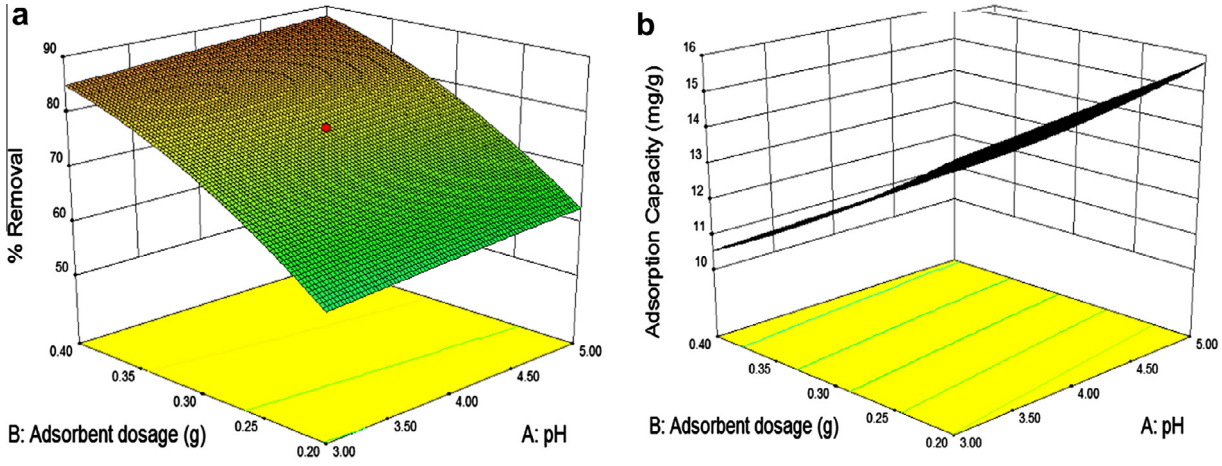

Figure 14 The combined effect of pH and adsorbent dosage on (a) percentage removal and (b) adsorption capacity of Phenol using RTIL encapsulated MCs.

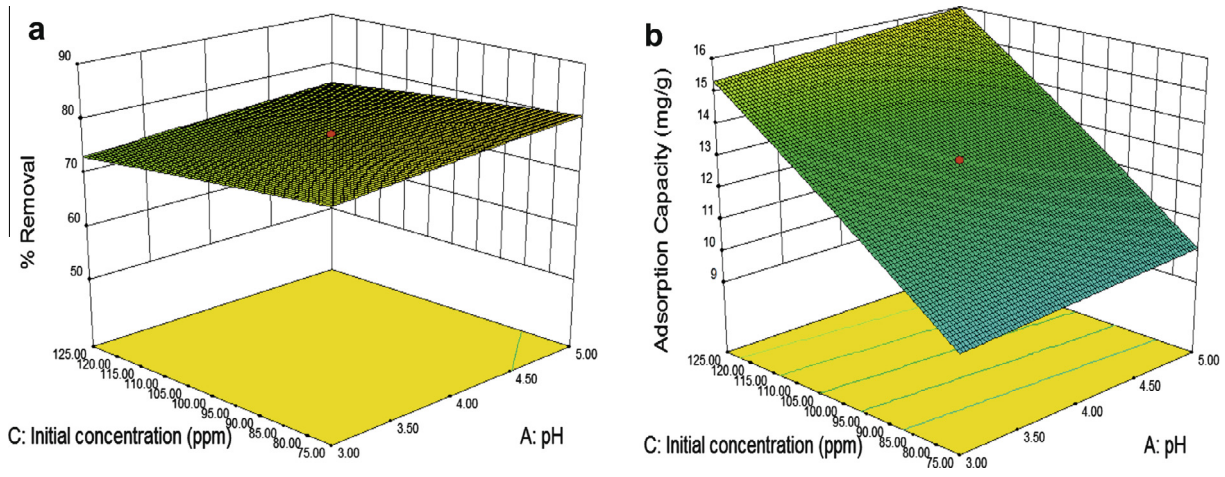

Figure 15 The combined effect of adsorbent dosage and initial concentration on (a) percentage removal and (b) adsorption capacity of Phenol using RTIL encapsulated MCs.

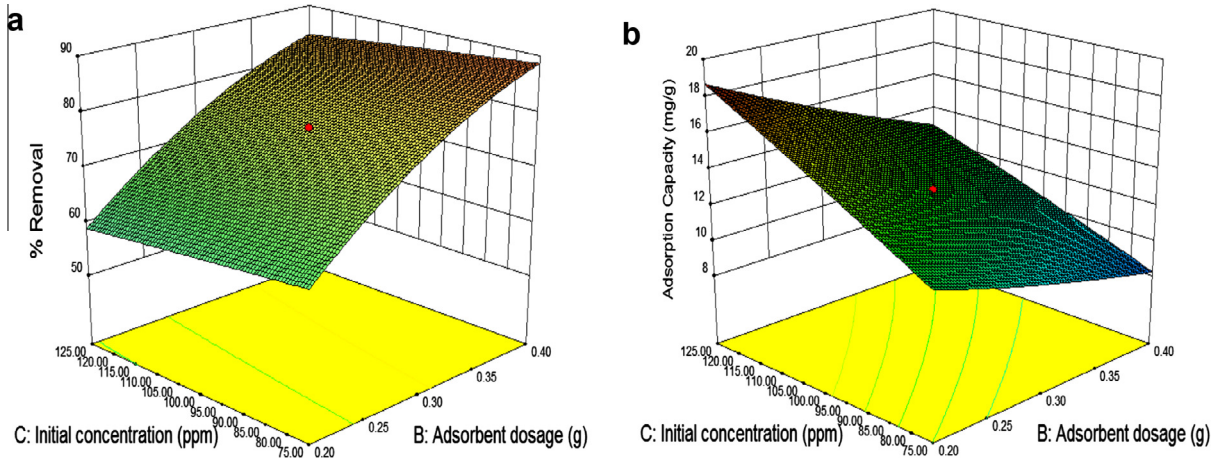

Figure 16 The combined effect of initial concentration and pH on (a) percentage removal and (b) adsorption capacity of Phenol using RTIL encapsulated MCs.

Table 8 Optimized process variable value for adsorption of phenol by RTIL encapsulated MCs.

Adsorbent dosage (g/100 ml)	Initial Metal Ion Concentration (mg/l)	pH	% Removal		Adsorption capacity (mg/g)	
			Predicted	Experimental	Predicted	Experimental
1.0	100	6	92.5	93	9.07	9.3

phenol increased with an increased adsorbent dosage. The decrease in adsorption capacity might be attributed to the shortage of metal ion concentration in the solution since the initial metal ion concentration was kept constant for all varying dosages. The increase in percentage removal may be due to the complete utilization of all active sites in the adsorbent dosage by metal ions. The maximum percentage removal of 89% and adsorption capacity of 8.2 mg/g at an initial concentration of 75 ppm and an adsorbent dosage of 0.4 g were obtained at a constant of pH 4.

3.5.3. The combined effect of initial metal ion concentration and pH

The combined effect of initial concentration and pH on percentage removal and adsorption capacity of phenol using RTIL encapsulated MCs is shown in Figs. 16(a) and (b) respectively. The adsorption capacity of Phenol increased with increased metal ion concentrations and the percentage removal of Phenol decreased with increased metal ion concentrations. This may be due to the availability of active sites which is sufficient to accommodate the metal ions at lower concentrations.

Table 9 Summary of parameters for various isotherm models.

Isotherm model	Equation	Values of constants
Langmuir isotherm	$\frac{C_e}{q_e} = \frac{1}{b.\theta} + \frac{C_e}{\theta}$	θ(mg g^{-1}) = 111.11, b (L mg^{-1}) = 1.5×10^3, R^2 = 0.888
Freundlich isotherm	$\ln q_e = \ln K + \frac{1}{n} \ln C_e$	$1/n$ = 0.955, K (mg g^{-1}) = 0.184, R^2 = 0.999
Temkin isotherm	$q_e = a + b \ln C_e$	b = 0.1998, a (1/g) = 4.06, R^2 = 0.848

where θ (mg/g) is the adsorption capacity, b is the energy of adsorption in Langmuir isotherm, n is indicative of bond energies between metal ion and the adsorbent, K is related to bond strength and a, b are Temkin constants in the Temkin isotherm.

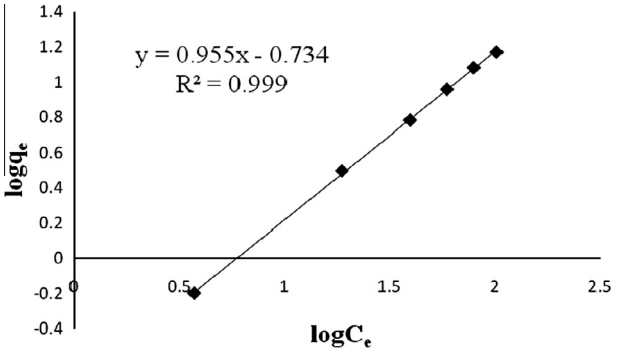

Figure 17 Freundlich isotherm for adsorption of phenol using RTIL encapsulated Mcs.

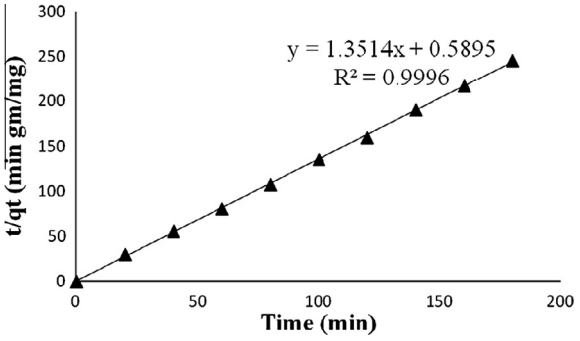

Figure 18 Pseudo second order kinetics for adsorption of phenol using RTIL encapsulated MCs.

The maximum percentage removal of 81% and adsorption capacity of 10.11 mg/g were achieved at an initial concentration of 75 ppm, at a pH of 5 and at a constant RTIL encapsulated MC dosage of 0.3 g.

The predicted and the experimental optimum conditions of the process variables for the maximum percentage removal and adsorption capacity are shown in Table 8.

3.6. Adsorption isotherms

Various isotherms like Freundlich, Langmuir, and Temkin were used to describe the equilibrium characteristics of adsorption of phenol by RTIL encapsulated MCs. The linearized form of isotherms (Uddin et al., 2007) and the value of different constants are given in Table 9.

The experimental data obtained at equilibrium condition fitted satisfactorily with Freundlich isotherm for adsorption of phenol using RTIL encapsulated MCs which reveals multilayer adsorption and is shown in Fig. 17.

3.7. Adsorption kinetics

The pseudo first order, pseudo second order and simple elovich kinetics models were tested to investigate the rate of adsorption process for phenol using RTIL encapsulated MCs. The linearized form of adsorption kinetics (Uddin et al., 2007) and their parameter values are given in Table 10. From Table 10, it is clear that the adsorption of phenol using RTIL encapsulated MCs followed the pseudo second order kinetics and is shown in Fig. 18

3.8. Thermodynamic studies

Thermodynamic considerations of the adsorption process are essential to conclude whether the process is spontaneous or not. The thermodynamic parameters, namely free energy (ΔG), enthalpy (ΔH) and entropy (ΔS) have an important role to determine spontaneity and heat change of the adsorption process. Thermodynamic distribution coefficient is defined as

Table 10 Summary of parameters for various kinetic models.

Kinetic model	Equation	Parameter constant	Value
Pseudo first order	$\ln(q_e - q_t) = \ln q_e - K_{1ad} t$	K_{1ad} (min^{-1})	9.718
		R^2	0.8026
Pseudo second order	$\frac{t}{q_t} = \frac{1}{K_{2ad} \cdot q_e^2} + \frac{t}{q_e}$	K_{2ad} (g mg^{-1} min)	3.098
		q_e(mg/g)	0.739
		R^2	0.9996
Simple Elovich	$q_t = \alpha + \beta \ln t$	β	0.716
		α	4.8588
		R^2	0.8625

where q_t is the adsorption capacity (mg/g), K_{1ad} is the pseudo-first-order rate constant in min-1, K_{2ad} is the pseudo-second-order rate constant in 1/mol.s and α, B is the simple elovich kinetic constants.

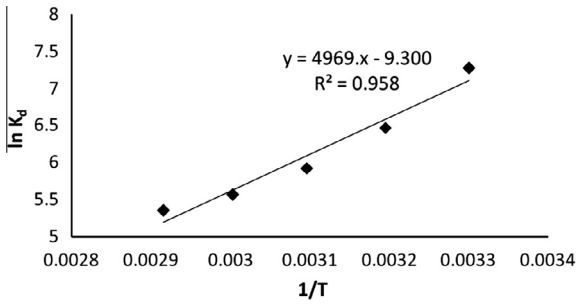

Figure 19 Effect of temperature on thermodynamic distribution coefficient.

$$K_{\mathrm{D}} = \frac{C_i - C_{eq}}{C_{eq} m} V \tag{4.11}$$

where K_{D} is the thermodynamic distribution coefficient, C_i is the initial concentration of solution, C_{eq} is the equilibrium concentration of solution, V is the volume of solution in ml, m is the mass of adsorbent in gm, From Vont Hoff''s equation we have

$$In K_{\mathrm{D}} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{4.12}$$

Hence, by plotting $\ln K_{\mathrm{D}}$ against $1/T$ as shown in Fig. 19 the values of entropy change and enthalpy change are evaluated as -77.32 kJ/kg K and -4.13×10^7 J/kg, respectively. The negative value of Gibbs free energy indicates the spontaneous nature of the adsorption of phenol by microcapsules.

4. Conclusions

Kinetic and adsorption isotherm studies revealed that RTIL encapsulated polymer microcapsules prepared using styrene and divinyl benzene as adsorbent can be effectively employed for the adsorption of phenol. It was found that phenol adsorption was dependent on pH. Adsorption of phenol follows the Freundlich isotherm of multilayer adsorption and obeys a pseudo-second order model. Thermodynamic analysis of the adsorption suggests that the process is not only exothermic but also spontaneous. Desorption studies indicated regeneration of the adsorbent for three cycles of operation and also the stability of the extractant in the microcapsules. Development of a mathematical model for phenol adsorption process simulation and optimization on the basis of statistical design of experiments appears to be a useful tool for predicting and understanding the interaction effects between experimental parameters. Response surface methodology and the central composite design were appropriate in determining the optimal conditions for phenol adsorption on RTIL encapsulated polymer microcapsules. The optimal conditions of adsorption established by RSM are as follows: initial phenol concentration: 100 ppm, pH: 6, adsorbent dosage: 1 g/100 ml. In these conditions the percentage removal of phenol and the adsorption capacity were 92.5% and 9.07 mg/g which are in good agreement with the predicted values.

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