Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2019.23697

147 (2019) 308–315
April

Optimization and equilibrium studies of phenol removal by modified Amberlite XAD-2 polymer using statistical optimization approach

Fozia K. Soomro[a], Saima Q. Memon[a,*], M.Y. Khuhawar[b]

[a]*M.A. Kazi Institute of Chemistry, University of Sindh, Jamshoro, Pakistan, emails: saimaqmemon@usindh.edu.pk (S.Q. Memon), foziasoomro@gmail.com (F.K. Soomro)*
[b]*Institute of Advance Research Studies in Chemical Sciences, University of Sindh, Jamshoro, Pakistan, email: mykhuhawar@usindh.edu.pk*

Received 10 March 2018; Accepted 27 December 2018

ABSTRACT

In the present study 1,4-benzenedicarboxyaldehyde-modified Amberlite XAD-2 (BDCA-XAD-2) polymer was synthesized and its removal efficiency for phenol from aqueous solution was investigated. Response surface methodology (RSM) with central composite design of statistical optimization is adopted to optimize removal efficiency. The RSM was used to determine the effect of amount of adsorbent, pH of adsorbate, initial concentration of adsorbate, contact time and the interaction effects of all these terms on removal efficiency. Regression coefficient (R^2 = 99.99%) of a plot of the predicted vs. the observed values confirms the applicability of the predicted model. The adsorption kinetics fitted well with pseudo-second-order model and the adsorption capacity of phenol was 592.3 mg g^{-1} onto BDCA-XAD-2 inferred from the Freundlich model.

Keywords: Removal optimization; Design of experiment; Modified XAD-2; Phenol removal

1. Introduction

Phenol, one of the priority organic pollutant, pollutes the water resources by discharge of various industries such as coal refineries, petrochemical, paper, pesticides and coal conversion [1–3]. Environmental Protection Agency has set a limit of 0.1 mg L^{-1} of phenol in wastewater [4–6] because of its solubility and acute toxicity. Treatment of phenol contaminated effluents prior to discharge is, therefore, a great environmental concern. Based on number of review articles published on removal of phenol, it can be concluded that adsorption is one of the most efficient treatment option [7–9]. Series studies have investigated that the polymeric adsorbents are better alternative to activated carbon silica gel and alumina for the removal of phenol from aqueous solutions [10–15]. Polymeric adsorbents exhibit striking characteristics such as chemical stability, large surface area, high equilibrium adsorption capacity, wide pore size distribution, excellent selectivity and structural diversity [16,17]. Chemical modification is a strategy widely used to enhance adsorption selectivity with additional benefit of increased adsorption capacities. Functional groups chemically introduced onto surface of the polymers are responsible for diverse chemical properties of adsorbent, different surface groups such as thiamine and diethylenetriamine are reported to have strong binding interactions with adsorbate [18–22]. In the best of our knowledge, there is little work done on modification of commercial Amberlite XAD-2 for removal of phenol. Present study is designed for chemical modification of commercial Amberlite XAD-2 polymeric resin by a simple modification route in order to enhance the adsorption capacity and selectivity of polymer for removal of phenol. Optimum removal parameters were obtained by statistical optimization method, that is, response surface methodology (RSM). RSM is useful for determining not only effect of each variable on response but, it also determines the interaction effect of variables [23–25]. Adsorption behavior of phenol on modified surface was evaluated by detailed equilibrium studies.

* Corresponding author.

2. Materials and methods

2.1. Chemicals and materials

All the chemicals used were of analytical grade. Amberlite XAD-2 (bead size 200–400 mesh, pore diameter 90–50 Å and surface area 300–750 $m^2 g^{-1}$) was purchased from Fluka (Germany). 1,4-Benzenedicarboxaldehyde was purchased from Alfa Aeser (Germany). HCl, NaOH and CH_3COOH/CH_3COONa were used for adjusting pH 2, 9 and 5.5, respectively, and were purchased from Merck (Germany). Deionized water was used throughout the study (Human Corporation. Seoul, Korea). The IR spectra were recorded using a, Thermo-Nicolet USA, FT-IR spectrometer. CHNS analyzer (PerkinElmer, USA) was used for elemental analysis. Quantification of phenol was carried on HPLC (Hitachi 655, Japan) using methanol: water (70:30) as solvent system, ZORBX Eclipse XDB-C-18, (4.6 × 150 mm, 5 um) column and UV detector (270 nm). Shaking of phenol solution with adsorbent was carried out using Irmeco GmbH (Germany) automatic thermostated shaker model 1–4000.

2.2. Modification of Amberlite XAD-2

Amberlite XAD-2 resin was washed with water and methanol and finally dried in an oven at 80°C for 12 h. XAD-2 was first modified into amino XAD-2 by reported procedure [26] as; The nitration of XAD-2 was carried by mixing 5.0 g of XAD-2 with 10 mL of concentrated HNO_3 and 25 mL of concentrated H_2SO_4 and stirred at 60°C for 1.0 h. Nitro XAD-2 was treated with mixture of 40 g of $SnCl_2$, 45 mL of concentrated HCl in 50 mL of ethanol solvent for 12 h at 90°C in N_2 atmosphere and was reduced to amino XAD-2. Finally, Amino XAD-2 and 1,4-benzenedicarboxaldehyde in methanol were refluxed at 60°C for 3 h to synthesize the modified BDCA-XAD-2 adsorbent. The final product was washed with distilled water and stored for further analysis. Fig. 1 shows the chemical route for conversion of XAD-2 into BDCA-XAD-2.

2.3. Experimental methods

Batch adsorption experiments were performed in a thermostated shaker at 25°C. Different weighed amounts of adsorbents (10–100 mg) were mixed with model solution (10–100 mg L^{-1}) of phenol at pH values 2–9. Mixtures were agitated for a period of 10–180 min at 150 rpm. The residual concentration of phenol was analyzed by HPLC. The % removal was calculated by Eq. (1).

$$\%\text{Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of phenol, respectively.

2.4. Factorial design of experiments

Statistical optimization of process parameters selected as independent variables including pH, phenol concentration, BDCA-XAD-2 amount and contact time. All the selected parameters were optimized for the removal of phenol from aqueous solution. Design of 18 experimental runs based on three levels were constructed and tried for removal of phenol. Preliminary trials were carried out in order to fix the level values of each factor. The range and levels of the experimental variables investigated in this study are shown in Table 1. Each parameter was coded at three levels: –1 (minimum), 0 (medium) and +1(maximum).

The response function describing the variations of dependent variable (percent removal efficiency) with four independent variables can be written as follows:

$$Y = b_0 + b_1A + b_2B + b_3C + b_4C + b_{11}A_2 + b_{12}AB + b_{13}AC + b_{14}AD + b_{22}B_2 + b_{23}BC + b_{24}BD + b_{33}C_2 + b_{34}CD + b_{44}D \quad (2)$$

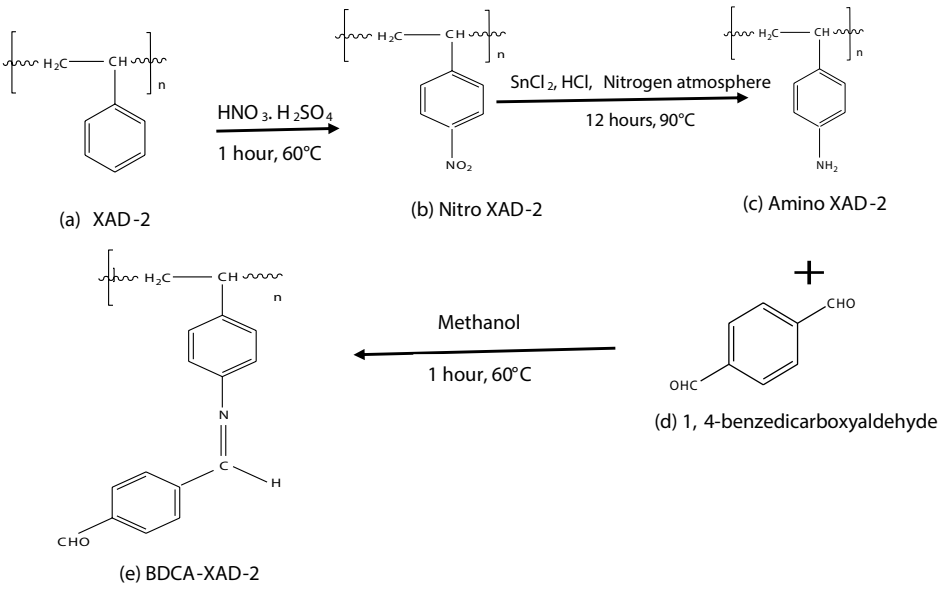

Fig. 1. Reaction scheme for modification of Amberlite XAD-2.

Table 1
Levels of factors used in experimental design for the removal of phenol

Factors	Code levels		
	–1	0	+1
Amount (mg), *A*	10	55	100
pH, *B*	2.0	5.5	9.0
Concentration (mg L^{-1}), *C*	10	55	100
Time (min), *D*	10	95	180

where *Y* is the measured response variable; *A*, *B*, *C* and *D* are the independent variables; b_1–b_4 are the first order coefficients; b_{12}–b_{34} are the interaction coefficients; b_{11}–b_{44} are the (pure) second-order coefficients and b_0 is the intercept (or constant term). The response function coefficients were determined by regression using Statgraphics plus 5.1 computer program.

2.5. Real sample analysis

Different real water samples were collected and potential of the adsorbent for phenol removal was estimated. Sample (S1) was collected from Kotri site area, Pakistan; sample (S2) was collected from Hyderabad site area Pakistan; sample (S3) was collected from Sukkur site area, Pakistan; sample (S4) was collected from Karachi site area and sample (S5) was collected from Multan site area, Pakistan.

3. Result and discussion

3.1. Characterization

Fig. 2 represents the FT-IR spectra of amino resin and BDCA-XAD-2. Three additional peaks at 2,866.38, 1,687.90 and 1,498.60 cm^{-1} in BDCA-XAD-2 spectra can be attributed to the stretching vibration of C–H, C=O and C=N, respectively. Appearance of these peaks supports the conversion of amino XAD-2 into BDCA-XAD-2. The formation of BDCA-XAD-2 was also confirmed by elemental analysis and percentages of elements obtained as C, 80.92%; H, 6.42%; N, 5.93%; O, 6.71% and theoretically calculated values for $C_{16}H_{15}NO$ are C, 80.98%; H, 6.37%; N, 5.90%; O, 6.74%. The CHNS analysis results confirmed the successful conversion of amino XAD-2 into BDCA-XAD-2.

3.2. Comparison of plain XAD-2 with functionalized XAD-2

Before detailed studies of functionalized resin, a study was carried out on un-modified XAD-2 for removal of phenol. Different parameters such as pH, time, volume and resin amount were optimized. The % removal at optimum conditions on un-modified XAD-2 was 40.15%. As the percentage removal was clearly very low and modification increases removal of phenol over 50%, we did not study the other parameters.

3.3. Statistical analysis

RSM is a statistical model that uses quantitative data from experiments for determination of regression equation constants and operating conditions [27]. For the present study, Draper-Lin small composite design has been used to develop a mathematical model. The experimental design work is given in Table 2, along with the experimental and predicted results for the removal of phenol onto BDCA-XAD-2.

A very close agreement between the values obtained by experiment and values predicted by model (Table 2) indicate the appropriateness of tested model for adsorption of phenol onto BDCA-XAD-2. The maximum percentage removal obtained was 95.23% onto BDCA-XAD-2.

3.3.1. Regression analysis

The statistical significance of the ratio of mean square variation due to regression and mean square residual

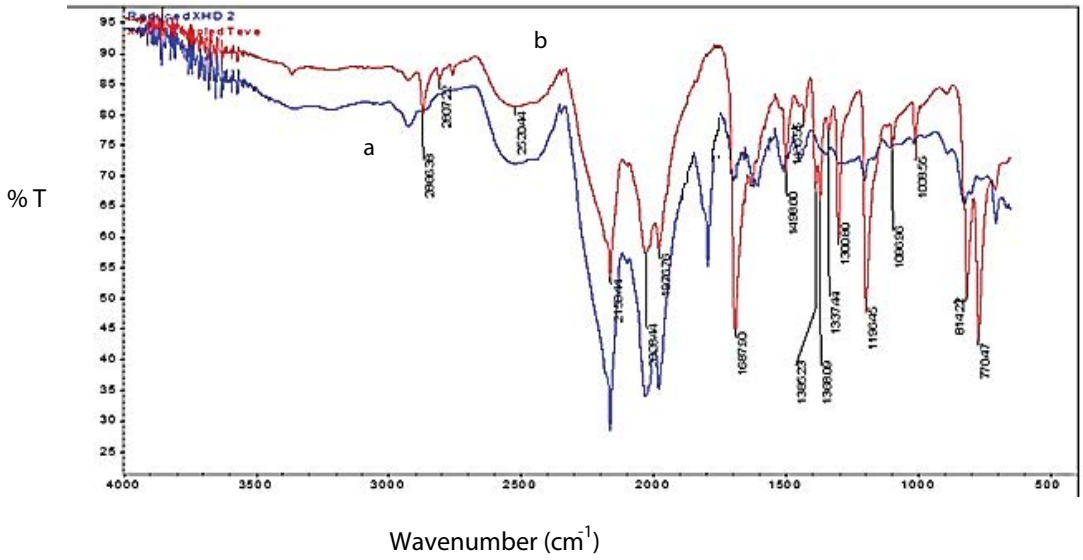

Fig. 2. FT-IR spectra of (a) Amino XAD-2, and (b) BDCA-XAD-2.

Table 2
Experimental design and results for % removal of phenol onto BDCA-XAD-2

Trails	Code values				% Removal onto BDCA-XAD-2	
	A	*B*	*C*	*D*	Observed (%)	Predicted (%)
1	–1	+1	–1	–1	55.02	52.24
2	–1	–1	–1	–1	59.62	58.97
3	0	0	+1	0	58.62	58.55
4	+1	+1	–1	–1	67.24	66.97
5	+1	+1	+1	–1	74.02	74.24
6	0	0	0	–1	52.32	51.95
7	–1	+1	+1	+1	48.45	48.44
8	+1	0	0	0	75.42	74.95
9	–1	+1	0	0	75.81	74.82
10	+1	+1	–1	+1	80.25	80.44
11	0	–1	0	0	74.43	74.87
12	+1	–1	+1	+1	95.23	95.76
13	–1	–1	+1	+1	49.12	48.87
14	0	0	–1	0	78.55	77.73
15	+1	0	0	0	45.12	54.05
16	0	0	0	+1	68.53	68.45
17	0	0	0	0	66.43	66.23
18	0	0	0	0	66.43	66.23

error was tested using the analysis of variance (ANOVA). A factor with a large *F*-ratio and small *p*-value (<0.05) is statistically considered to be significant [28,29]. The accuracy of the model checked from the corresponding ANOVA for the phenol removal, the obtained results are presented in Table 3 for BDCA-XAD-2. For the present case, the effect of terms; concentration, adsorbent amount and time were found to be highly significant because the *p*-values were less than 0.05. Variables: concentration and pH, and interaction terms: amount and time, pH and time have an antagonistic relationship with the removal of phenol. Whereas terms: amount, time, and interaction terms: amount and pH, amount and concentration, pH and concentration, time and concentration have synergistic effect. Furthermore, the high values R^2 (99.98% and 99.96%) and R^2 adjusted (99.95% and 99.94%) are very close to 1, indicating a high significance of the models for BDCA-XAD-2.

Finally, a regression equation was prepared using the values of coefficients, which are as follows:

$$\begin{aligned}\%\ \text{Removal} = {} & 70.9406 + 0.54882 \times A - 8.42028 \times B - 0.669254 \times C + 0.294002 \times D - \\ & 0.00307524 \times A^2 + 0.00642857 \times A \times B + 0.00369753 \times A \times C - \\ & 0.00123203 \times A \times D + 0.703889 \times B^2 + 0.0110317 \times B \times C - \\ & 0.00306723 \times B \times D + 0.000998835 \times C^2 + 0.000839869 \times \\ & C \times D - 0.000834236 \times D^2 \end{aligned} \quad (3)$$

3.3.2. Interpretation of residual plots

Fig. 3 is the plot of residuals vs. the predicted values, the residual is a difference between the observed and the predicted values [30]. All the residuals are randomly scattered around the zero, showing that the errors have a constant variance and confirmed the fitting of the model.

Table 3
ANOVA for % removal of phenol on BDCA-XAD-2

Sources	% Removal of phenol on BDCA-XAD-2	
	F-Ratio	*p*-Value
A: Amount	605.60	0.0001
B: pH	0.01	0.9190
C: Concentration	254.95	0.0005
D: Time	184.42	0.0009
AA	132.60	0.0014
AB	11.11	0.0446
AC	121.53	0.0016
AD	48.14	0.0061
BB	254.22	0.0005
BC	32.72	0.0106
BD	9.02	0.0575
CC	13.99	0.0333
CD	22.37	0.0179
DD	124.22	0.0015

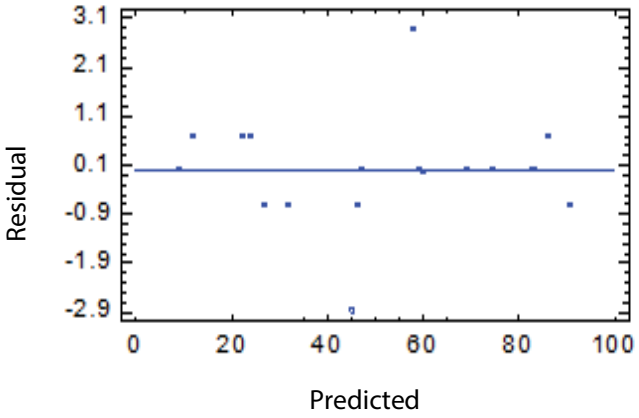

Fig. 3. Residuals plots for model validation for % removal of Phenol onto BDCA-XAD-2.

3.3.3. Student t test

In order to determine whether the calculated effects were significantly different from zero, Student's t test was employed. The evaluations are illustrated by means of Pareto charts in Fig. 4. The vertical line indicates the minimum statistically significant effect magnitude for a 95% confidence level. The values shown in the horizontal columns are Student's t test values for each effect. Any term that extend beyond this references line is considered significant. Positive sign shows direct relation with response function and negative sign shows inverse relation with response function. From the chart, it is demonstrated that the amount of adsorbents is highly and positively significant.

3.3.4. 3D Response surface plots

The 3D response surface graphs showed the combined effect of any two independent variables on the % removal

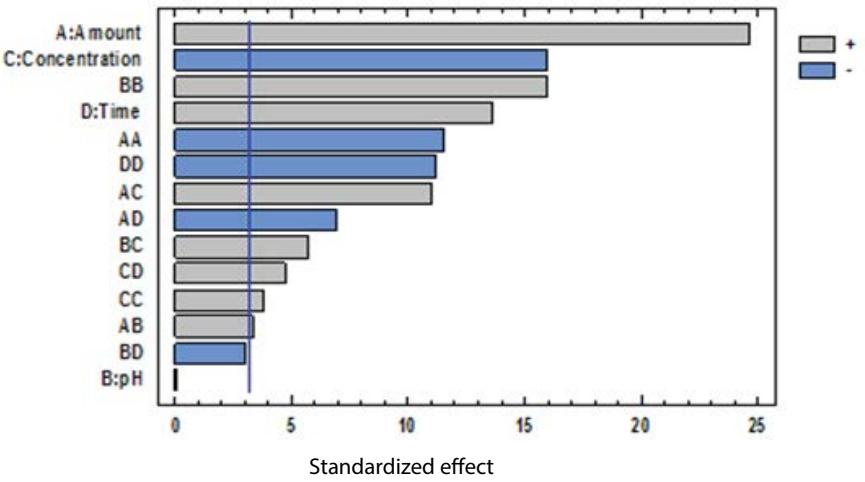

Fig. 4. Pareto chart of statistical effects on the % removal of phenol onto BDCA-XAD-2.

of phenol while other two independent variables are held at their optimized values, Figs. 5(a)–(c) show the 3D graphs of % removal of phenol onto BDCA-XAD-2. It can be seen from the plots that amount and time have positive effect on the removal; maximum removal is obtained between 120 and 150 min (Fig. 5(b)). Decrease in removal can be observed with increasing concentration of phenol (Fig. 5(c)) with optimum at 10 mg L^{-1}. Table 4 shows the minimum and maximum values taken for each variable along with the values predicted by software as optimum, when the desired value of response, that is, % removal was set at 100. The removal obtained at predicted optimum variable was 99.61%. Fig. 5(a) presents the combined effect of amount and pH on the % removal of phenol at optimum concentration of phenol 10 mg L^{-1} and time 123 min. The % adsorption of phenol increases with an increase in and decreases with increasing pH of phenol solution. The concentration of negatively charged phenoxide ions increases at high pH values and thus the repulsive forces between negatively charged phenol and adsorbent will reduce % adsorption at higher pH values. The mechanism of sorption can be deduced from this experiment by taking into account the condensation reaction between aldehyde group onto the surface and phenol in acidic medium [31]. The combined effect of amount and time is plotted in Fig. 5(b) at optimum concentration 10 mg L^{-1} and pH 2; % adsorption increase with increase in both amount and time. By increasing the amount of adsorbent, the surface area and availability of active sites increases for the removal of phenol. Fig. 5(c) shows the combined effects of concentration and time at optimum amount 72 mg and pH 2; % adsorption increases with decreasing initial phenol concentration and increasing reaction time. This is mainly due to availability of limited adsorption sites at higher concentration of adsorbate.

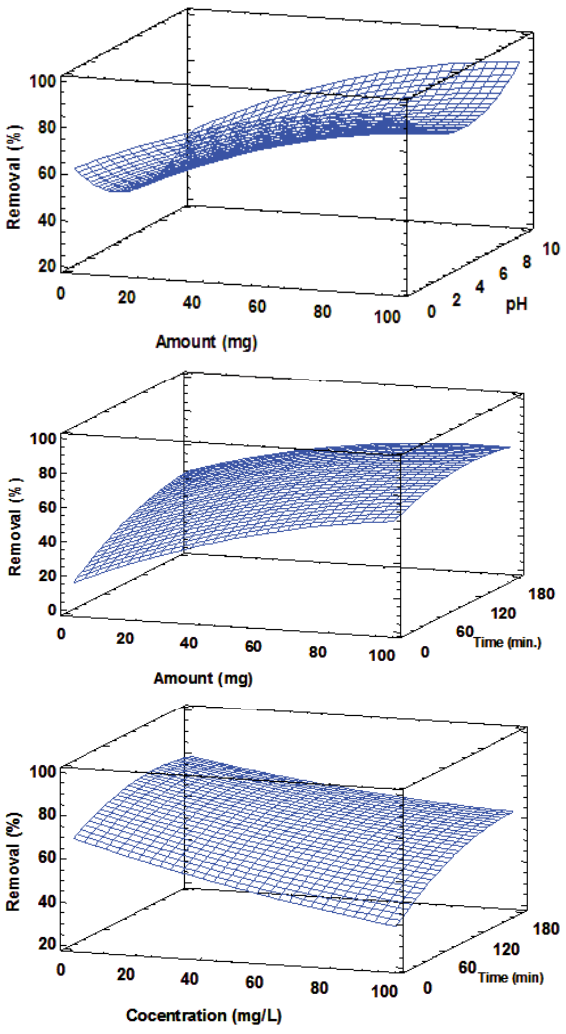

Fig. 5. 3D plots for combined effects of variables: (a) amount and pH; (b) amount and time; and (c) concentration and time on % adsorption of phenol on BDCA-XAD-2.

3.4. Isotherms studies

Mechanism of adsorption and the understanding of adsorption process can be obtained from equilibrium studies. The equilibrium data at equilibrium amount of adsorbed

Table 4
Optimum values obtained by CCD model

Factor	Low	High	Optimum
Amount (mg)	10.0	100.0	72
pH	2.0	9.0	2.0
Concentration (mg L^{-1})	10.0	100.0	10.0
Time (min)	10.0	180.0	125

Optimum value = 99.61% removal

phenol onto BDCA-XAD-2 and the concentration of phenol in the liquid phase C_e at constant temperature were used to describe the optimum isotherm model. The linear form of Langmuir, Freundlich and D–R isotherms was employed to describe the equilibrium data. The performance of each model was judged through correlation coefficient (R^2). The linear form of Langmuir, Freundlich and D–R equations are represented by Eqs. (4)–(6), respectively.

$$\frac{C_e}{C_{\text{ads}}} = \frac{1}{Qb} + \frac{C_e}{Q} \tag{4}$$

$$\log C_{\text{ads}} = \log K_F + \frac{1}{n}\log C_e \tag{5}$$

$$\ln C_{\text{ads}} = \ln K_{D-R} - \beta\varepsilon^2 \tag{6}$$

where C_{ads} is the amount of phenol adsorbed on adsorbent (mg g^{-1}); C_e is the equilibrium molar concentration of the phenol (mg L^{-1}) while Q, K_F and $K_{\text{D–R}}$ are Langmuir, Freundlich and D–R maximum adsorption capacity (mg g^{-1}), respectively; b is the Langumir constant related to the monolayer adsorption affinity of the binding sites (L g^{-1}), $1/n$ is Freundlich constant, β is related to the mean free energy of adsorption per mole of the adsorbent when it is transferred from infinite distance in the solution to the surface of the solid, and ϵ is Polanyi potential and is equal to $RT \ln (1 + 1/C_e)$, where T is temperature and R is general gas constant (J mol^{-1} K^{-1}).

The parameters of tested isotherm models are summarized in Table 5. The result indicates that the linear form of Freundlich and D–R isotherms model fit well with the experimental data as indicated by the high values of the regression coefficients R^2. However, the standard error of estimate calculated for both isotherms, Freundlich and D–R isotherm, was 0.07 and 2.5, respectively, showing the better fit of data to Freundlich isotherm. On the other hand, the exponent n refers to as the adsorption intensity and is an indicator of favorableness of the adsorbent/adsorbate system. In general $n > 1$ suggests that adsorbate is favorably adsorbed on the adsorbent. The higher the n value, the stronger the adsorption intensity [32]. The value of E indicates the nature of adsorption, that is, when E > 8–16 kJ mol^{-1} sorption is considered as chemical or ion exchange in nature but when its value is <8 kJ mol^{-1} it is considered as physisorption [33]. The value of energy of adsorption calculated for removal of phenol using BDCA-XAD-2 was 9.32 kJ mol^{-1} which shows ion-exchange nature of adsorption.

3.5. Kinetic study

In order to evaluate the kinetic parameters, experimental data obtained were fitted to different kinetic models namely the pseudo-first-order, pseudo-second-order and intra-particle diffusion models. The reliability of these kinetic models was determined by measuring the coefficients of determination (R^2).

Eqs. (7)–(9) represent the linear form of pseudo-first-order and pseudo-second-order and intra-particle diffusion rate equations as follows:

$$\ln q_e - q_t = \ln q_e - K_F t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{K_s q_e^2} + \frac{1}{q_e} t \tag{8}$$

$$q_t = k_{ip} t^{1/2} + c \tag{9}$$

where K_f is pseudo-first-order rate constant, q_e and q_t are the amount of phenol (mg g^{-1}) at equilibrium and at time t, respectively. K_s is pseudo-second-order rate constant and K_{ip} is the intra-particle diffusion rate constant.

The kinetic parameters are summarized in Table 6. For the pseudo-second-order, the correlation coefficient close to unity and experimental q_e similar to the q_e calculated from pseudo-second-order indicates that adsorption kinetics of phenol is described well by pseudo-second-order model.

3.6. Comparison capacities with reported methods for phenol adsorption

Table 7 compares the adsorption capacities for the removal of phenol with modified XAD-based adsorbents [9,12,16–18,34,35], commercial XAD-based adsorbents [36–39] and BDCA-XAD-2. Adsorption capacity of BDCA-XAD-2 is comparable even better with most of the adsorbents, whereas

Table 5
Adsorption isotherm parameters and correlation coefficient for the adsorption of phenol onto BDCA-XAD-2

Adsorbent	Langmuir				Freundlich			D–R		
	Q (mg g^{-1})	b (L g^{-1})	R_L	R^2	K_F (mg g^{-1})	$1/n$	R^2	$K_{\text{D–R}}$ (mg g^{-1})	E (kJ mol^{-1})	R^2
BDCA-XAD-2	138.0	4.3×10^3	0.01–0.9	0.987	592.3	0.7	0.999	141	9.32	0.999

Table 6
Kinetic parameters for the pseudo-first-order, pseudo-second-order and intra-particle diffusion of phenol onto BDCA-XAD-2

Adsorbent	Pseudo-first-order			Pseudo-second-order			Intra-particle diffusion		$q_{e,exp}$ (mg g^{-1})
	K_f (min^{-1})	R^2	q_e (mg g^{-1})	K_s (g mg^{-1} min^{-1})	R^2	q_e (mg g^{-1})	K_{ip} (mg g^{-1} min^{-1})	R^2	
BDCA-XAD-2	–0.0206	0.972	5.05	0.050	0.999	12.66	0.198	0.987	12.53

Table 7
Comparison capacities of phenol onto modified polymer adsorbents

Polymer	Chemical modifier	Capacity mg g^{-1}	Reference
Styrene-co-divinylbenzene	Aminophosphinic acid	158	18
Styrene-co-divinylbenzene	Carboxylic acid	208	18
Chloromethylated poly(styrene-codivinylbenzene)	Aminated NDA-101	14.4	12
Chloromethylated poly(styrene-codivinylbenzene)	Aminated NDA-103	15.3	12
Chloromethylated polystyrene	Formaldehyde carbonyl	169	34
XAD-4	Phenol α,α'-dichloro-p-xylene	97.5	35
XAD-4	4,4′-Bis(chloromethyl)-1,1′-biphenyl	127	35
Hypercrosslinked PS resin	Diethylenetriamine	202	9
Chloromethylated poly(styrene-co-divinylbenzene)	N-methylacetamide	199	17
XAD-4	Carbon tetrachloride XAD-4-I	80.6	16
XAD-4	Benzoyl chloride XAD-4-II	94.8	16
Commercial XAD-4	–	0.06	36
Commercial XAD-7	–	78.7	37
Commercial XAD-16	–	0.14	38
Amberlite IRA-420	–	315	39
BDCA-XAD-2	1,4-Benzenedicarboxyaldehyde	592	This work

Table 8
Removal of phenol from real water samples

Sample	Concentration (mg L^{-1}) of phenol	% Removal of phenol	RSD (%)
*S*1	3.52	95	1.7
*S*2	5.34	78	1.6
*S*3	4.62	87	2.4
*S*4	4.45	86	2.5
*S*5	3.83	93	1.9

its synthesis required only simple reagents and the method is also energy saving.

3.7. Resin regeneration and reuse

Desorption of adsorbed phenol was tested with different volumes and concentrations of organic solvents. Recovery of phenol was found more than 98% with 5 mL of 80% of methanol, and after five times reuse, only 5% decrease in efficiency of BDCA-XAD-2 adsorbents was observed.

3.8. Removal of phenol from real samples

The optimum adsorption parameters calculated from model were applied for the treatment of phenol contaminated water from different industrial streams in Pakistan. The % removal of phenol up to 95% was obtained as shown in Table 8. This shows the efficacy of synthesized resin for real matrices application.

4. Conclusion

XAD-2 was chemically modified by 1,4-benzenedicarboxyaldehyde and successfully applied for efficient removal of toxic phenol from aqueous solutions and real water samples. Statistical optimization approach was conducted to optimize the process parameters. The Freundlich model correlated well with the adsorption mechanism and kinetics of phenol adsorption better followed pseudo-second-order.

References

[1] S.M. Nowee, M. Taherian, M. Salimi, S.M. Mousavi, Modeling and simulation of phenol removal from wastewater using a membrane contactor as a bioreactor, Appl. Math. Modell., 42 (2017) 300–314.
[2] M.D. Victor-Ortega, J.M. Ochando-Pulido, A. Martinez-Ferez, Phenols removal from industrial effluents through novel polymeric resins: kinetics and equilibrium studies, Sep. Purif. Methods, 160 (2016) 136–144.
[3] M. Yanga, Y. Huanga, Q. Yuea, H. Cao, X. Lia, Y. Lin, Preparation of a novel polymeric adsorbent and its adsorption of phenol in aqueous solution, Desal. Wat. Treat., 57 (2016) 13295–1330.

[4] A. Garba, N.S. Nasrib, H. Basria, R. Ismaild, Z.A. Majid, U.D. Hamza, J. Mohammed, Adsorptive removal of phenol from aqueous solution on a modified palm shell-based carbon: fixed-bed adsorption studies, Desal. Wat. Treat., 57 (2016) 29488–29499.
[5] L. Zhang, B. Zhang, T. Wu, D. Sun, Y. Li, Adsorption behavior and mechanism of chlorophenols onto organo clays in aqueous solution, Colloids Surf. A Physicochem. Eng. Asp., 484 (2015) 118–129.
[6] D. Peredo-Mancilla, H. Dominguez, Adsorption of phenol molecules by sodium dodecyl sulfate (SDS) surfactants deposited on solid surfaces, a computer simulation study, J. Mol. Graphics Modell., 65 (2016) 108–112.
[7] L.G.C. Villegas, N. Mashhadi, M. Chen, D. Mukherjee, K.E. Taylor, N. Biswas, A Short review of techniques for phenol removal from wastewater, Curr Pollut. Rep., 2 (2016) 157–167.
[8] S. Mohammadi, A. Kargari, H. Sanaeepur, K. Abbassian, A. Najafi, E. Mofarrah, Phenol removal from industrial wastewaters: a short review, Desal. Wat. Treat., 53 (2015) 2215–2234.
[9] A. Mittal, M. Teotia, R.K. Soni, J. Mittal, Applications of egg shell and egg shell membrane as adsorbents: a review, J. Mol. Liq., 223 (2016) 376–387.
[10] I. Ipek, N. Kabay, M. Yuksel, Separation of bisphenol A and phenol from water by polymer adsorbents: equilibrium and kinetics studies, J. Water Process Eng., 16 (2017) 206–211.
[11] B.C. Pan, Y. Xiong, Q. Su, A.M. Li, J.L. Chen, Q.X. Zhang, Role of amination of a polymeric adsorbent on phenol adsorption from aqueous solution, Chemosphere, 51 (2003) 953–962.
[12] W. Zhang, Q. Du, B. Pan, L. Lv, C. Hong, Z. Jiang, D. Kong, Adsorption equilibrium and heat of phenol onto aminated polymeric resins from aqueous solution, Colloids Surf. A Physicochem. Eng. Asp., 346 (2009) 34–38.
[13] M. Caetano, C. Valderrama, A. Farran, J.L. Cortina, Phenol removal from aqueous solution by adsorption and ion exchange mechanisms onto polymeric resins, J. Colloid Interface Sci., 338 (2009) 402–409.
[14] C.G. Oh, J.H. Ahn, S.K. Ihm, Adsorptive removal of phenolic compounds by using hypercrosslinked polystyrenic beads with bimodal pore size distribution, React. Funct. Polym., 7 (2003) 103–111.
[15] A. Li, Q. Zhang, J. Chen, Z. Fei, C. Long, W. Li, Adsoption of phenolic compounds on Amberlite XAD-4 and its acetylated derivative MX-4, React. Funct. Polym., 49 (2001) 225–233.
[16] C. Li, M. Xu, X. Sun, S. Han, X. Wu, Y.N. Liu, J. Huang, S. Deng, Chemical modification of Amberlite XAD-4 by carbonyl groups for phenol adsorption from wastewater, Chem. Eng. J., 229 (2013) 20–26.
[17] J. Huang, X. Jin, S. Deng, Phenol adsorption on an N-methylacetamide-modified hypercrosslinked resin from aqueous solutions, Chem. Eng. J., 192 (2012) 192–200.
[18] C. Paurariu, G. Mihoc, A. Popa, S.G. Muntean, R. Ianos, Adsorption of phenol and p-chlorophenol from aqueous solutions on poly (styrene-co-divinylbenzene) functionalized materials, Chem. Eng. J., 222 (2013) 218–227.
[19] T.A. Saleh, S.O. Adio, M. Asif, H. Dafalla, Statistical analysis of phenols adsorption on diethylenetriamine-modified activated carbon, J. Cleaner Prod., 182 (2018) 960–968
[20] S.B. Moshe, G. Rytwo, Thiamine-based organoclay for phenol removal from water, Appl. Clay Sci., 155 (2018) 50–56.
[21] G. Xiao, R. Wen, P. You, D. Wu, Adsorption of phenol onto four hyper-cross-linked polymeric adsorbents: effect of hydrogen bonding receptor in micropores on; adsorption capacity, Microporous Mesoporous Mater., 239 (2017) 40–44.
[22] X. Wang, X. Mao, J. Hung, Hierarachal porous hyper-cross-linked polymer modified with phenolic hydroxyl groups and their efficient adsorption of aniline from aqueous solution, Colloids Surf. A Physicochem. Eng. Asp., 558 (2018) 80–87.
[23] Z. Noorimotlagh, S. Shahriyar, R. Darvishi, C. Soltani, R. Tajik, Optimized adsorption of 4-chlorophenol onto activated carbon derived from milk vetch utilizing response surface methodology, Desal. Wat. Treat., 57 (2016) 14213–14226.
[24] D. Bingol, D. Saraydin, D.S. Ozbay, Full factorial design approach to Hg (II) adsorption onto hydrogel, Arabian J. Sci. Eng., 40 (2015) 109–116.
[25] U.T. Un, F. Ates, N. Erginel, O. Ozcan, E. Oduncu, Adsorption of Disperse Orange 30 dye onto activated carbon derived from Holm Oak (Quercus Ilex) acorns: a 3k factorial design and analysis, J. Environ. Manage., 155 (2015) 89–96.
[26] S.Q. Memon, S.M. Hasany, M.I. Bhanger, M.Y. Khuhawar, Enrichment of Pb (II) ions using phthalic acid functionalized XAD-16 resin as a sorbent, J. Colloid Interface Sci., 291 (2005) 84–91.
[27] M. Saad, H. Tahir, J. Khan, U. Hameed, A. Saud, Synthesis of polyaniline nanoparticles and their application for the removal of Crystal Violet dye by ultrasonicated adsorption process based on response surface methodology, Ultrason. Sonochem., 34 (2017) 600–608.
[28] B. Kakavandi, M. Jahangiri-rad, M. Rafiee, A.R. Esfahani, A.K. Babaei, Development of response surface methodology for optimization of phenol and p-chlorophenol adsorption on magnetic recoverable carbon, Microporous Mesoporous Mater., 231 (2016) 192–206.
[29] A.N. Siyal, S.Q. Memon, M.I. Khaskheli, Optimization and equilibrium studies of Pb(II) removal by Grewia asiatica seed: a factorial design approach, Polish J. Chem. Technol., 14 (2012) 71—77.
[30] A. Rathinam, J.R. Rao, B.U. Nair, Adsorption of phenol onto activated carbon from seaweed: determination of the optimal experimental parameters using factorial design, J. Taiwan Inst. Chem. Eng., 42 (2011) 952–956.
[31] S. Udayakumar, S. Ajaikumar, A. Pandurangan, Electrophilic substitution reaction of phenols with aldehydes: enhance the yield of bisphenols by HPA and supported HPA, Catal. Commun., 8 (2007) 366–374.
[32] X. Zeng, T. Yu, P. Wang, R. Yuan, Q. Wen, F. Yunge, C. Wang, R. Shi, Preparation and characterization of polar polymeric adsorbents with high surface area for the removal of phenol from water, J. Hazard. Mater., 177 (2010) 773–780.
[33] S.M. Hasany, M.M. Saeed, M. Ahmed, Sorption of traces of silver ions onto polyurethane foam from acidic solution, Talanta, 54 (2001) 89–98.
[34] X. Li, Y. Liu, D. Di, G. Wang, Y. Liu, A formaldehyde carbonyl groups-modified self-crosslinked polystyrene resin: synthesis, adsorption and separation properties, Colloids Surf. A Physicochem. Eng. Asp., 500 (2016) 1–9.
[35] J. Huang, L. Yang, X. Wu, M. Xu, Y.N. Liu, S. Deng, Phenol adsorption on α α'-dichloro-p-xylene(DCX) and 4,4′-bis(chloromethyl)-1,10-biphenyl (BCMBP) modified XAD-4 resins from aqueous solutions, Chem. Eng. J., 222 (2013) 1–8.
[36] A.M. Li, Q.X. Zhang, G.C. Zhang, J.L. Chen, Z.H. Fei, F.Q. Liu, Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent, Chemosphere, 47 (2002) 981–989.
[37] B.J. Pan, B.C. Pan, W.M. Zhang, Q.R. Zhang, Q.X. Zhang, S.R. Zheng, Adsorptive removal of phenol from aqueous phase by using a porous acrylic ester polymer, J. Hazard. Mater., 157 (2008) 293–299.
[38] K. Abburi, Adsorption of phenol and p-chlorophenol from their single and bisolute aqueous solutions on Amberlite XAD-16 resin, J. Hazard. Mater., B105 (2003) 143–156.
[39] M. Carmona, A.D. Lucas, J.L. Valverde, B. Velasco, J.F. Rodrıguez, Combined adsorption and ion exchange equilibrium of phenol on Amberlite IRA-420, Chem. Eng. J., 117 (2006) 155–160.