

Removal of phenol from aqueous solution using Duolite-A-171 Duolite-A-368 plus and Duolite-S-861 polymeric resins

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Abstract: The removal of phenol from aqueous solution was evaluated by batch method using two ion exchange resins, Duolite-A-171 (DLE-171) (a strong anion exchange resin) and Duolite-A-368 plus (DLE-368) (a weak anion exchange resin) and a nonfunctionalized Duolite-S-861 (DLE-861) resin. The maximum removal capacity was achieved at pH 11. The removal of phenol was found to be in the following order DLE-171 > DLE-368 > DLE-861. The mechanism involved in the process was found to be both adsorption and ion exchange. The resin was characterized using FTIR and SEM with EDAX analysis. The equilibrium data were fitted to Freundlich isotherm. The kinetics of the sorption was found to follow pseudo-second-order and intraparticle diffusion models. The values of thermodynamic parameters indicate the nature of sorption is spontaneous and exothermic.

Key Words: Removal of Phenol; Polymeric Resins; Duolite-A-171; Duolite-A-368; Duolite-S-171.

1. INTRODUCTION:

Heavy metals are recognized as the persistent and toxic environmental contaminants. Phenol is widely used for the commercial production of a wide variety of resins, including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications. Phenolic pollutants occur in wastewater of a number of industries, such as high temperature coal conversion, petroleum refining, resin and plastics etc. Such aromatic hydroxyl compounds are considered as priority pollutants since they are harmful to organisms especially human and also to aquatic life, at low concentrations and can be toxic when present elevated levels and are known or suspected to be carcinogens [1]. Phenol decomposition is difficult due to, principally, its stability and its solubility in water. Phenol and substituted phenols have a half life time between 2 and 72 days. They have a strong and unpleasant smell which makes the contaminated water totally unusable [2]. Phenol finds its way in to the environment through industrial effluents and is present in very high amounts in several industrial effluents, which makes its removal a must. Due to the toxic nature of phenol several regulatory bodies all over the globe like the Ministry of Environment and Forests (MOEF), Government of India and EPA, USEPA have listed phenol and phenolic compounds on the priority-pollutants list as well as also have proposed maximum permissible limits of phenol in different categories of water. Chronic toxic effects due to phenols reported in humans include vomiting, difficulty in swallowing, anorexia, liver and kidney damage, headache, fainting and other mental disturbances. Phenol being highly toxic and difficult to degrade biologically, it has led to setting up of rigid limits on the acceptable level of phenol in the environment. Table 1 represents the maximum permissible limits of phenol in different categories of water [3-6].

1.1. Adsorption of phenol by resins

In recent years an increasing interest has been focused on various type of adsorbents for the treatment of heavy metal ions from industrial effluents because they are environmental friendly and potentially inexpensive [7-11]. Adsorption by resin is one of the most frequently used methods to remove phenolic compounds from water, because resins possess perfect adsorption ability for that class of compounds. In recent years, the use of polymeric resins in removal of phenolic compounds has also been widely studied due to its better mechanical strength and feasible regeneration. Factors, such as temperature, pH and sorbent characteristics have a great influence by use of this technique. Owing to the formation of phenolate ions, the removal of phenol compounds by non-ionic and some synthetic polymeric resins has shown a lower capacity than that of activated carbon at alkaline medium. The uptake or removal of phenolic compounds could be enhanced by using anionic resins by ion-exchange in addition to adsorption at alkaline medium. Moreover, the polymeric resins can be easily regenerated using organic

reagents and thus, the polymeric resins are considered as the potential alternative for the extensively studied activated carbon.

2. EXPERIMENTAL:

2.1. Materials

The resins DLE-171, DLE-368 and DLE-861 were supplied by Auchtel Products Ltd., Mumbai, India. The typical properties of the resins are given in Table 2. Phenol with 99% pure and other chemicals employed were of analytical grade and purchased from Central Drug House (P) Ltd, New Delhi, India. Ultra pure water was used throughout the study. The materials purchased were used without further purification.

2.2. Sorption experiments

For the sorption experiments, about 0.1 g of the adsorbents was accurately weighed and added to 50 ml of phenol aqueous solution of 10 mg/L as initial concentration at pH 11. The contents in the flask were then shaken thoroughly using a thermostated shaker rotating at a speed of 200 rpm. The solution was then filtered after 60 min and the residual phenol concentration was measured by using UV Visible spectrophotometer (Pharo 300 Merck) at 287 nm. pH measurements were carried out with the expandable ion analyzer EA 940 with pH electrode. The pH of the working solution was adjusted by adding 0.1 M of HCl/NaOH solution. The sorption capacity of the sorbents was studied at different conditions including various dosages of sorbent, contact time, pH of the medium and the effect of anions for the optimization. The equilibrium capacity of phenol on the adsorbent was calculated as:

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

where C_0 is the initial concentration (mg/L), C_e is the phenol concentration at equilibrium time (mg/L), V is the volume of the aqueous solution (L) and W is the weight of the resin (g). The percentage removal of phenol was calculated as follows:

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

2.3. Effect of Contact Time

The contact time of adsorbent with adsorbate is of great importance in adsorption since contact time depends on the nature of the system used. Adsorption experiments for phenol on DLE -171, DLE-368 and DLE-561 were carried out as follows: To each of 0.1 g the resins, 50 mL of solution containing 10 mg L⁻¹ of phenol were added. The samples were shaken at room temperature for periods ranging from 15 min to 120 min, and then filtered and residual concentration of phenol is measured.

2.4. Effect of pH

The pH of the aqueous solution is a significant controlling factor in adsorption process, in order to optimize the pH for maximum removal efficiency; the effect of pH on the removal of phenol is investigated by varying the pH values from 1 to 12 at a temperature of 30 ± 2°C and for fixed phenol concentration of 10 mg L⁻¹. The contact time has been fixed at 1 h for all experiments. The sorption capacity of the DLE -171, DLE-368 and DLE-561 resins were obtained.

2.5. Effect of the Amount of Adsorbent

Under optimum conditions of shaking time and pH, the effect of adsorbent dosage on the removal of phenol at 10 mg L⁻¹ was also studied by shaking 50 mL of phenol solution with 0.050 to 0.250 g of the adsorbent.

2.6. Effect of anions

Drinking water contains several common anions such as, Cl⁻, SO₄²⁻, HCO₃⁻ and NO₃⁻ along with phenol. These common anions can compete with the phenol during the adsorption process and hence, the dependence of sorption capacity on to these resins was investigated in the presence of common anions at pH 11. The experiments

were carried out in the presence of common anions with affixed initial concentration of 200 mg/L by keeping 10 mg/L as the phenol initial concentration at pH 11.

2.7. Characterization

FTIR spectra (JASCO-60 plus) of the sorbent were recorded using KBr pellets in the range of 400–4000 cm^{-1} . Scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX) (VEGA3 TESCAN) was used to characterize the surface morphology of the composite before and after the sorption of Pb(II) ions. Elemental analysis for the composite was evaluated using EDX. Computations were made using Microcal Origin software. The effectiveness of fit was discussed using regression correlation coefficient (r), standard deviation (sd) and chi-square (χ^2) analysis.

2.8. Adsorption isotherms

The two most widely used isotherms namely Freundlich and Langmuir models have been adopted to describe the equilibrium established between adsorbed phenol on the sorbent (q_e) and the remaining phenol in the solution (C_e) at 303, 313 and 323 K with different initial concentrations (10 mg/L, 20 mg/L, 30mg/L, 40 mg/L and 50 mg/L). The heterogeneous multilayer coverage governs the Freundlich isotherm model and the homogeneous monolayer coverage governs the Langmuir isotherm model with equivalency of sorption sites. The linear form of isotherms are represented by Eqs (3) and (4),

Freundlich isotherm

$$\log q_e = \log k_F + 1/n \log C_e \quad (3)$$

Langmuir isotherm

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (4)$$

where q_e is the amount of phenol adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of phenol in solution (mg/L), k_F is the measure of adsorption capacity and $1/n$ is the adsorption intensity. Q^0 is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent and b (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption.

The essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter, R_L [12].

$$R_L = 1/1+bC_0 \quad (5)$$

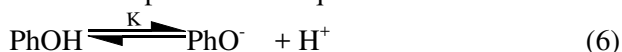
where b (L/mg) is Langmuir isotherm constant and C_0 (mg/L) is initial phenol concentration.

3. RESULTS AND DISCUSSION:

Adsorption of phenol onto DLE-171, DLE-368 and DLE-861 was carried out as a function of pH, contact time, dosage and salts. The sorption capacities are given as the units of sorbed phenol quantity per kg of sorbent (mg/kg).

3.1. Effect of pH of the medium

It has been identified that the pH of the working solution is the most critical parameter which affects the removal of phenol from aqueous solution. The dissociation of phenol in aqueous solution is as follows



Phenol exists in molecular form in the range of $\text{pH} \leq 7$. The ion fraction of PhO^- increases with increase of pH and predominates in alkaline medium at $\text{pH} > 10.5$. Fig.1 shows the effect of pH on the removal of phenol at different solution pH. The uptake of phenol by the polymeric resins increases with increase in pH and reached maximum at pH 11. Due to the formation of PhO^- , anion exchange mechanism was considered to be involved in the removal of phenol process in addition to molecular adsorption at alkaline pH. The uptake of phenol started to decrease at above pH 11, due to the competitive adsorption of OH^- ions.

3.2. Effect of contact time

Contact time is the amount of time required before adsorption process becomes constant and equilibrium is reached. The experiments were carried out at 200 rpm, 100 mg/50 ml sorbent dose at 25°C, pH 11 and 10 mg/L

as initial phenol concentration for different time intervals up to 120 min. Fig. 2 shows the effect of contact time on the adsorption of the phenol on to DLE-171, DLE-368 and DLE-861 under the given experimental conditions. The adsorption of phenol on to these resins attained equilibrium after 60 min and no remarkable changes were observed for longer contact time. Therefore, the optimum contact time for the removal of phenol by these resins is fixed as 60 min for the further adsorption studies.

3.3. Effect of dosage

Increasing the amount of sorbent dose resulted, as expected, in increase in the phenol removal capacity. The experiments were carried out with varying amount of sorbent dose (50 mg to 300 mg) keeping other parameters such as pH 7, 10 mg/L as initial phenol concentration, 200 rpm and 60 min contact time at 25°C as constant. Fig. 3 shows the adsorption capacity of phenol onto these resins as a function of sorbent dosage at the given experimental conditions. It is clear to see that the sorption capacity increase with increase in sorbent dosage which is obvious due to increase in the number of active sites. The plot of sorption capacity shows that the removal of phenol was high at lower dosages where as reduced at higher dosages. This may be due to the fact that the adsorption sites remain unsaturated during the removal process. Hence, 100 mg of sorbent was fixed as the optimum dosage for the further adsorption studies.

3.4. Effect of anions

Drinking water contains several common anions such as, Cl^- , SO_4^{2-} , HCO_3^- and NO_3^- along with phenol. These common anions can compete with the phenol during the adsorption process and hence, the dependence of sorption capacity on to these resins was investigated in the presence of common anions at pH 11. The experiments were carried out in the presence of common anions with affixed initial concentration of 200 mg/L by keeping 10 mg/L as the phenol initial concentration at pH 11. Fig. 4 shows the effect of common anions on the adsorption capacity of these resins under given experimental conditions. The reduction in the sorption capacity may due to the competition among the anions for the sites on the sorbent surfaces, which is decided by the concentration, charge and size of the anions.

3.5. Characterization of the sorbents

Fig. 5 and Fig. 6 depict the FTIR spectra of the DLE-171 and DLE-368 resins before and after phenol sorption respectively. Before sorption of the phenol by the DLE-171 resin, a band at 3442 cm^{-1} , represents a strong and broad band of the O-H stretching vibrations. The bands at 3018 , 2922 and 2858 cm^{-1} are corresponds to the symmetric/asymmetric, stretching vibrations of the ring C-H bonds and CH_2 groups of the resin matrix respectively. A band at 1615 cm^{-1} corresponds to the vibration of the O-H group of the water molecule present in the resin. The bands observed at 976 and 826 cm^{-1} are related to the deformation vibrations of 1, 4 disubstituted benzene ring present in the styrene- divinylbenzene of the resin matrix [13-16]. The quaternary ammonium group present in the resin is confirmed by the bands at 1488 to 1463 cm^{-1} , symmetric deformation and asymmetric angular bending of methyl groups of quaternary nitrogen $-\text{N}^+(\text{CH}_3)_3$ and N- CH_3 bending at 1494 cm^{-1} [17-19]. Even after sorption of phenol, the bands and their positions on the spectra are very similar to those before sorption, but the intensity of a few bands changed after the sorption process. The SEM pictures of DLE-171 resin before and after phenol adsorption are shown in Fig.7a, 7b and 7c. The change in the SEM micrographs of DLE-171 and phenol-sorbed DLE-171 indicates the structural changes of the sorbent. The EDAX spectrum of phenol sorbed DLE-171 is also shown in Fig.6d.

3.6. Sorption isotherms

The two most widely used isotherms namely Freundlich and Langmuir have been adopted to describe the adsorption characteristics of DLE-171, DLE-368 resins for the removal of phenol. The adsorption capacity of DLE-861 for the removal of phenol was found to be very less and hence, further studies were limited to DLE-171, DLE-368 resins.

3.6.1. Freundlich isotherm

The linear form of Freundlich isotherm is represented as follows,

$$\log q_e = \log k_F + 1/n \log C_e \quad (7)$$

Where q_e is the amount of phenol adsorbed per unit weight of the sorbent (mg/g), C_e is the equilibrium concentration of phenol in solution (mg/L), k_F is the measure of adsorption capacity and $1/n$ is the adsorption intensity were calculated from the slope and intercept of the plot $\log q_e$ vs $\log C_e$ (Figure 8) and the values are listed in Table 3. The values of k_F decreases with increase in temperature suggesting that the phenol uptake by both DLE-171 and DLE-368 resins is an exothermic process. The magnitude of the exponent $1/n$ lies between 0 and 1, and the values of n greater than 1 indicates the favourable conditions for the adsorption [20]. The linear plot with higher correlation coefficient (r) values shows that the Freundlich isotherm fits with the experimental data of both DLE-171 and DLE-368 resins.

3.6.2. Langmuir isotherm

The linear form of the Langmuir isotherm is represented by

$$C_e/q_e = 1/Q^0 b + C_e/Q^0 \quad (8)$$

where Q^0 is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent and b (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption. A linear plot is obtained for the sorbent when C_e/q_e is plotted against

C_e (Figure 9) which gives Q^0 and b values from the slope and intercept respectively and the calculated results are listed in Table 3. The slight decrease in the values of Q^0 with increasing temperature confirms the preference for low temperature for adsorption which further confirms the exothermic nature of the sorption process. The correlation coefficient (r) > 0.9 indicates the applicability of the isotherm, the essential characteristics of the Langmuir isotherm can be expressed in terms of the dimensionless constant separation factor or equilibrium parameter R_L [13].

$$R_L = 1/1+bC_0 \quad (9)$$

The R_L values at different temperatures studied were calculated and are listed in Table 3. The R_L values lying between 0 and 1 indicated that the conditions were favorable for adsorption. The higher r values of Freundlich over Langmuir isotherm indicated the suitability of Freundlich isotherm than the Langmuir isotherm.

3.6.3. Chi-square analysis

Chi-square analysis was carried out to identify the suitable isotherm for sorption of phenol onto DLE-171 and DLE-368 resins. The mathematical expression for chi-square analysis is as follows;

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \quad (10)$$

where $q_{e,m}$ is equilibrium capacity obtained by calculating from the model (mg/g) and q_e is experimental data on the equilibrium capacity (mg/g). If data from the model are similar to the experimental data, χ^2 will be a small number, while if they differ, χ^2 will be a bigger number. The χ^2 values for DLE-171 and DLE-368 resins were tabulated in Table 3. The lower χ^2 -values of Freundlich isotherm indicate the better applicability for the phenol sorption on DLE-171 and DLE-368 resins.

3.7. Thermodynamic treatment of phenol sorption process

Thermodynamic parameters associated with the adsorption, viz., standard free energy change (ΔG^0), standard enthalpy change (ΔH^0) and standard entropy change (ΔS^0) were calculated as follows;

The change in free energy of sorption is given by:

$$\Delta G^0 = -RT \ln K_0 \quad (11)$$

where K_0 is the sorption distribution coefficient, ΔG^0 is the standard free energy change of sorption (kJ mol^{-1}), T is the temperature in Kelvin and R is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$). The sorption distribution coefficient K_0 was determined from the slope of the plot $\ln(q_e/C_e)$ against C_e at different temperatures and extrapolating to zero C_e according to Khan and Singh method [14].

The sorption distribution coefficient can be expressed in terms of ΔH^0 and ΔS^0 as a function of temperature:

$$\ln K^0 = \Delta S^0/R - \Delta H^0/RT \quad (12)$$

where ΔH^0 is the standard enthalpy change (kJ mol^{-1}) and ΔS^0 is standard entropy change ($\text{kJ mol}^{-1} \text{ K}^{-1}$). The values of ΔH^0 and ΔS^0 can be obtained from the slope and intercept of a plot of $\ln K_0$ against $1/T$. Calculated thermodynamic parameters are presented in Table 4.

The calculated values of thermodynamic parameters are shown in Table 4. The negative values of ΔG^0 confirm the spontaneous nature of phenol sorption. The value of ΔH^0 is negative indicating that the sorption process is exothermic. The negative value of ΔS^0 which is a measure of randomness at the solid/liquid interface during phenol sorption indicates that the phenol sorption is reversible.

3.8. Sorption dynamics

Two main types of sorption kinetic models, viz., reaction based and diffusion based models were employed in order to investigate the adsorption process of phenol on to DLE-171 and DLE-368 resins.

3.8.1. Reaction-based models

The most commonly used pseudo-first-order kinetic model [14] is given as

$$\log(q_e - q_t) = \log q_e - k_{ad}t/2.303 \quad (13)$$

where q_t is the amount of phenol on the surface of the resins at time t (mg/g) and k_{ad} is the equilibrium rate constant of the pseudo-first-order sorption (min^{-1}). The linear plots of $\log(q_e - q_t)$ against t gives straight line indicate the applicability of pseudo-first-order model. The slope of the straight line plot of $\log(q_e - q_t)$ against t at three different temperatures, viz., 303, 313 and 323 K give the value of the pseudo-first-order rate constant (k_{ad}) and r of DLE-171 and DLE-368 resins and are listed in Table 6 and 7 respectively.

In addition, the pseudo-second-order model is also widely used. There are four types of linear pseudo-second-order kinetic models [15], the most popular linear form is

$$t/q_t = 1/h + t/q_e \quad (14)$$

where $q_t = (q_e^2 kt)/(1 + q_e kt)$, the amount of phenol on the surface of the resins at any time, t (mg/g), k is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$), q_e is the amount of phenol sorbed at equilibrium (mg/g) and the initial sorption rate, $h = kq_e^2$ ($\text{g mg}^{-1} \text{ min}^{-1}$). The value of q_e (1/slope), k (slope²/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/q_t against t . The values of q_e , k , h and r of the pseudo-second-order model were obtained from the plots of t/q_t against t for phenol sorption at three different temperatures, viz., 303, 313 and 323 K of DLE-171 and DLE-368 resins and are presented in Table 5 and 6 respectively. The values of q_e decreases with increase in temperature indicating phenol sorption decreases with the rise in temperature. The higher r values obtained for the pseudo-second-order model than the pseudo-first-order indicating the applicability of the pseudo-second-order model for the phenol sorption onto the DLE-171 and DLE-368 resins.

3.8.2. Diffusion - based models

For a solid-liquid sorption process, the solute transfer is usually characterized either by particle diffusion or by intraparticle diffusion control.

A simple equation for the particle diffusion controlled sorption process is given as follows,

$$\ln(1 - C_t/C_e) = -k_p t \quad (15)$$

Where k_p is the particle rate constant (min^{-1}), The value of particle rate constant is obtained by the slope of the plot $\ln(1 - C_t/C_e)$ against t .

The intra particle diffusion model used here refers to the theory proposed by Weber and Morris [20] and its equation is

$$q_t = k_i t^{1/2} \quad (16)$$

Where k_i is the intraparticle rate constant ($\text{mg/g min}^{0.5}$). The slope of the plot of q_t against $t^{1/2}$ will give the value of intraparticle rate constant.

The values of k_p , k_i and r for the DLE-171 and DLE-368 resins are presented in Table 5 and 6 respectively. The higher r values obtained by intra particle diffusion model than the particle diffusion model for DLE-171 resin indicate the possibility of sorption process is being controlled by intra particle diffusion process where as in DLE-368 resin, the higher r values obtained for both particle diffusion and intra particle diffusion models suggest that the phenol diffusion on DLE-368 resin follows both the models, but better fits to intra particle diffusion model.

3.9. Mechanism of phenol sorption

The mechanism of phenol removal by DLE-171 and DLE-368 is governed by both adsorption and ion-exchange. The removal of phenol by these resins was found to be low up to pH 10 which is mainly governed by adsorption. The removal of phenol was found to be higher at pH 11 for these resins which is mainly governed by both adsorption and ion exchange [21]. The mechanism involved in the removal of phenol by DLE-171 resin is as followed:

Adsorption mechanism



Ion exchange mechanism



In the case of nonfunctionalized DLE-861 resin the phenol uptake is mainly governed by the van der Waals interaction between the aromatic ring of the phenol molecule and the resin matrix [21]

4. CONCLUSIONS:

In this study, the ability of removal of phenol by two ion exchange resins and nonfunctionalized resin was investigated under various equilibrium and thermodynamic conditions. DLE-171 resin displayed higher removal capacity at pH 11 than the other two resins namely DLE-368 and DLE-861. The sorption capacity of the resins was influenced by pH of the medium. The nature of the sorption process was spontaneous and exothermic. The removal of phenol on DLE-171 and DLE-368 resins followed Freundlich isotherm. The kinetics of the reaction follows pseudo-second-order and intraparticle diffusion models. The mechanism of phenol removal by DLE-171 and DLE-368 resins was mainly governed by both adsorption and ion exchange.

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Table 1. Maximum permissible limits of phenol in water

Agency	Types of Water	Maximum Permissible limit	Reference
USEPA	Wastewater	0.1 ppm	[3]
BIS	Drinking water	1.0 ppb	[3], [4]
WHO	Drinking water	1.0 ppb	[3], [5]
MoEF	Industrial effluent	1.0 ppm	[5], [6]

Table 2. Properties of the resins

Contents	Duolite-A-171plus	Duolite-A-368	Duolite-S-861
Matrix	Styrene-divinyl benzene copolymer	Cross linked polystyrene	Adsorbent grade resin
Functional group	-N-(CH ₃) ₃	-N(R) ₂ , Min 85% of TEC	Non functionalized
Ionic form as supplied	Cl ⁻	OH ⁻	-
Particle size	0.3 to 1.2 mm	0.3 to 1.2 mm	-
Physical form	Opaque beads	Ivory beads	White opaque beads
Moisture holding capacity	54-60%	35-60%	60-70%
Specific gravity	About 1.06	About 1.05	About 1.02
Packing density	650 to 700 g/L	680 g/L	-

Table 3. Freundlich and Langmuir isotherms of the resins

Resin	Temp. (K)	Freundlich isotherm					Langmuir isotherm				
		1/n	n	k _F (mg/g) ^{1/n} (L/mg)	r	χ ²	Q ^o (mg/g)	b (L/g)	R _L	r	χ ²
DLE-171	303	0.868	1.151	2.854	0.999	0.008	80.256	0.034	0.367	0.981	40.24
	313	0.869	1.150	2.619	0.999	0.013	76.335	0.033	0.376	0.987	11.26
	323	0.866	1.154	2.351	0.999	0.046	75.301	0.029	0.063	0.971	10.25
DLE-368	303	0.8907	1.122	1.938	0.999	0.022	86.430	0.021	0.080	0.993	35.33
	313	0.8962	1.115	1.450	0.999	0.018	82.918	0.016	0.093	0.979	8.79
	323	0.8971	1.114	1.212	0.999	0.023	80.321	0.013	0.066	0.980	8.41

Table 4. Thermodynamic parameters of the resins

Thermodynamic parameters	DLE - 171	DLE - 368
ΔG ^o (kJ mol ⁻¹)		
303 K	-8.02	-9.95
313 K	-9.34	-10.91
323 K	-9.25	-11.02
ΔH ^o (kJ mol ⁻¹)	-142.43	-6.32
ΔS ^o (kJ mol ⁻¹ K ⁻¹)	-0.47	-0.05

Table 5. Kinetic models of DLE -171 resins.

Kinetic models	Parameters	303 K					313 K				
		10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L	10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Pseudo-first-order	k _{ad} (min ⁻¹)	0.074	0.073	0.073 00	0.090	0.084	0.060	0.110	0.079	0.072	0.132
	r	0.993	0.930	0.913	0.987	0.992	0.914	0.935	0.897	0.988	0.963
	sd	0.753	0.263	0.295	0.133	0.093	0.242	0.379	0.355	0.099	0.332
Pseudo-second-order	q _e (mg/g)	4.629	8.735	13.95 4	19.75	23.63	4.310	8.996	14.551	19.091	21.824
	k (g/mg min)	0.036	0.032	0.007	0.004	0.004	0.068	0.018	0.005	0.004	0.007
	h (mg/g min)	0.775	2.495	1.466	1.639	2.399	1.281	1.527	1.128	1.657	3.715
	r	0.999	0.999	0.996	0.991	0.999	0.999	0.999	0.996	0.998	0.999
	sd	0.161	0.054	0.127	0.139	0.033	0.186	0.081	0.118	0.062	0.033
Particle diffusion	k _p (min ⁻¹)	0.110	0.100	0.145	0.134	0.131	0.116	0.082	0.115	0.060	0.064
	r	0.951	0.869	0.790	0.930	0.941	0.834	0.986	0.825	0.990	0.981
	sd	0.744	1.189	2.360	1.112	0.985	1.605	0.250	1.655	0.241	0.192
Intraparticle diffusion	k _i (mg/g min ^{0.5})	0.295	0.363	1.015	1.585	1.832	0.185	0.563	1.211	1.542	1.357
	r	0.917	0.957	0.960	0.944	0.953	0.920	0.911	0.943	0.957	0.934
	sd	0.244	0.208	0.560	1.047	1.106	0.149	0.484	0.806	0.881	0.979

Kinetic models	Parameters	323K				
		10 mg/L	20 mg/L	30 mg/L	40 mg/L	50 mg/L
Pseudo-first-order	$k_{ad}(\text{min}^{-1})$	0.075	0.062	0.2281	0.115	0.234
	R	0.970	0.852	0.848	0.933	0.759
	Sd	0.168	0.345	1.292	0.403	1.826
Pseudo-second-order	$q_e(\text{mg/g})$	4.784	8.389	12.933	16.345	23.446
	$k(\text{g/mg min})$	0.019	0.023	0.0141	0.017	0.002
	$h(\text{mg/g min})$	0.438	1.644	2.367	4.770	1.489
	R	0.996 0.997996	0.997	0.998	0.999	0.968
	Sd	0.353	0.177	0.097 0.097	0.017	0.231
Particle diffusion	$k_p(\text{min}^{-1})$	0.106	0.085	0.059	0.045	0.032
	R	0.910	0.802	0.972	0.99	0.968
	Sd	1.017	1.330	0.300	0.135	0.171
Intraparticle diffusion	$k_i(\text{mg/g min}^{0.5})$	0.390	0.433	0.674	0.676	1.834
	R	0.920	0.938	0.959	0.947	0.954
	Sd	0.314	0.304	0.378	0.432	1.095

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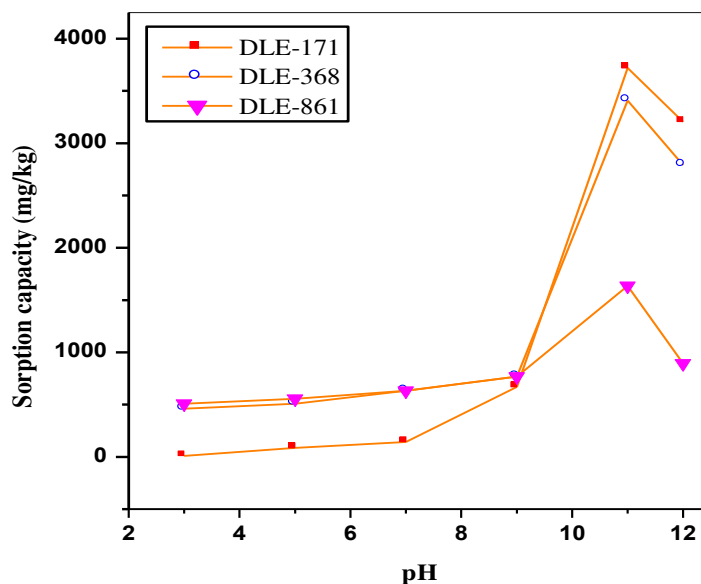


Fig. 1. Effect of pH on the removal capacity of phenol.

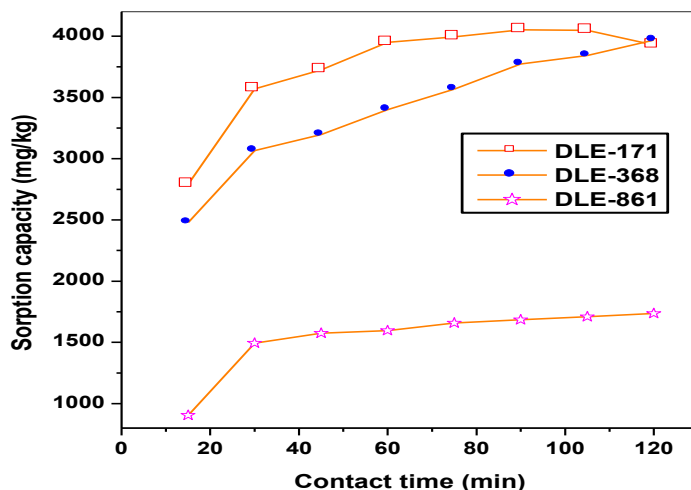


Fig. 2. Effect of contact time on the removal capacity of phenol.

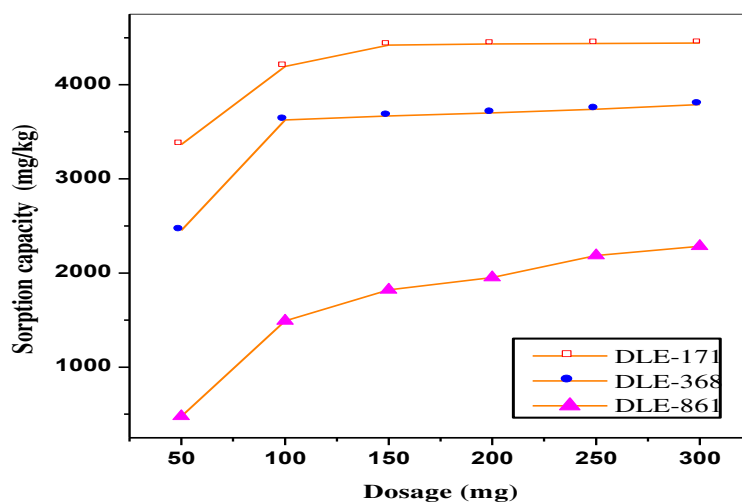


Fig. 3. Effect of dosage on the removal capacity of phenol.

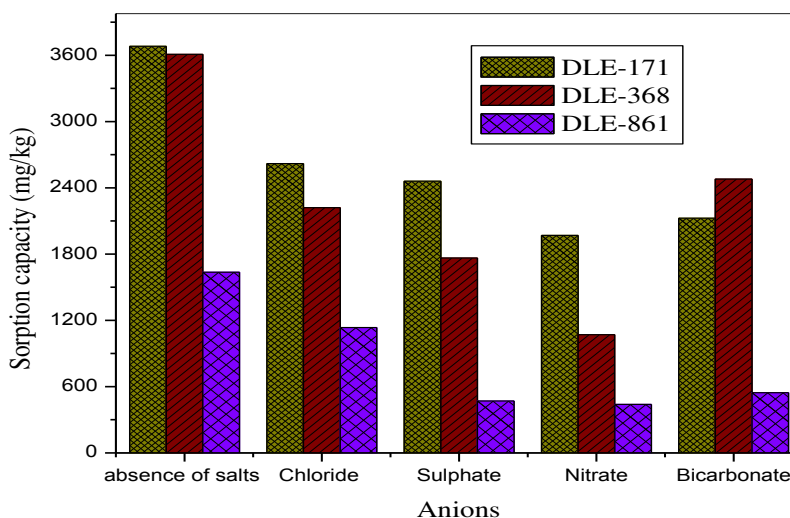


Fig. 4. Effect of anions on the removal capacity of phenol.

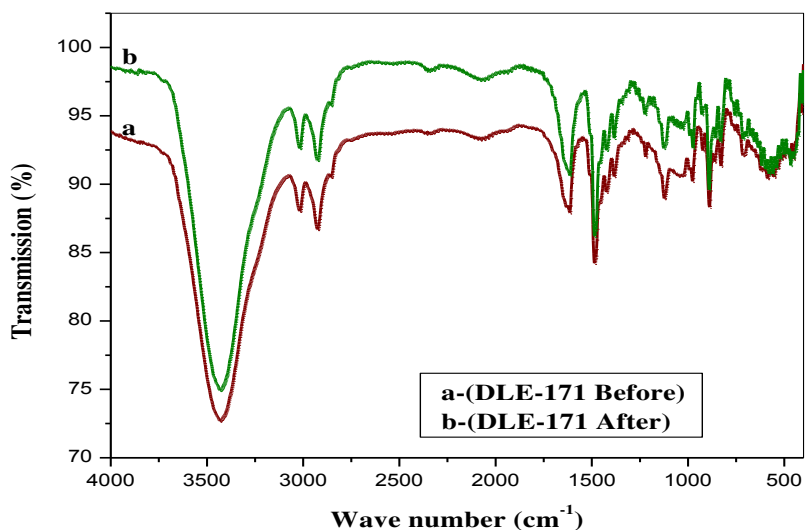


Fig. 5. FTIR spectra of (a) DLE-171 resin and (b) phenol sorbed DLE-171 resin.

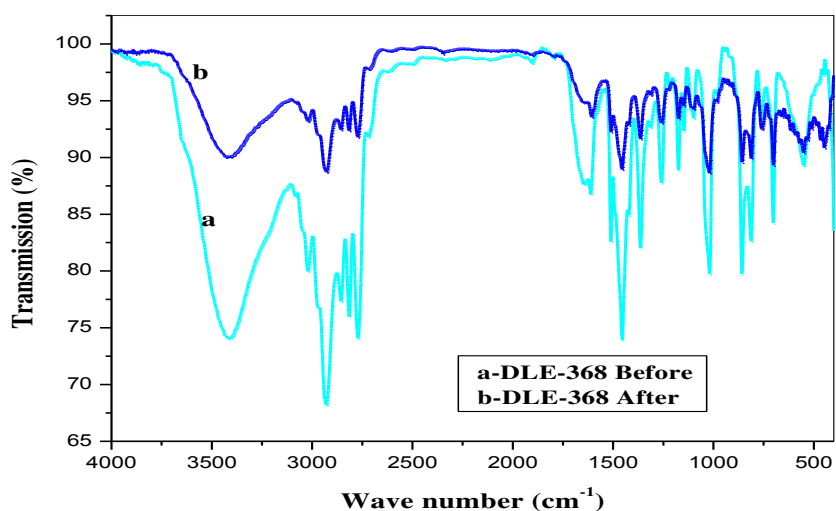


Fig. 6. FTIR spectra of (a) DLE-368 resin and (b) phenol sorbed DLE-368 resin.

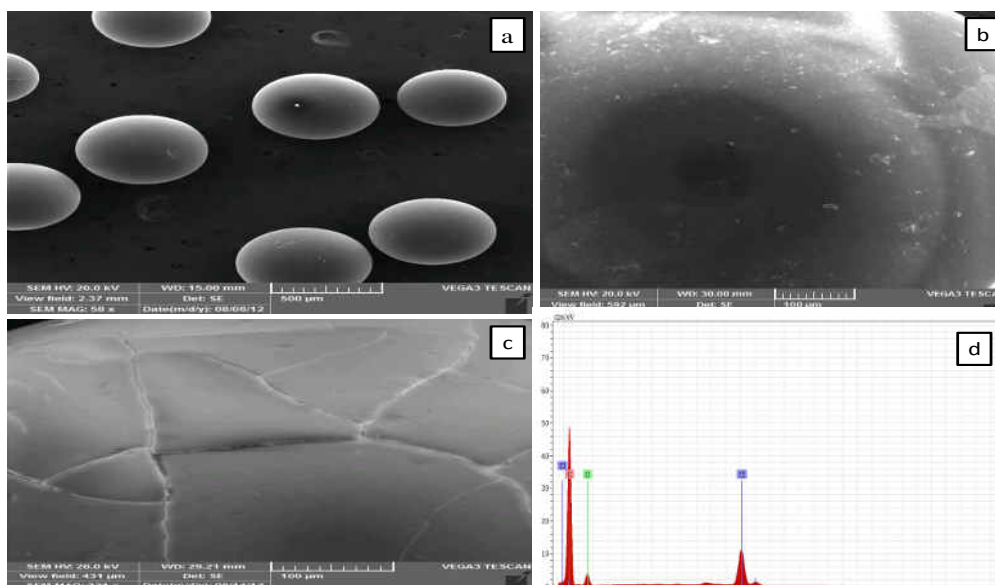


Fig.7. SEM images of DLE-171 (a) and (b) before phenol adsorption, (c) After phenol adsorption. EDAX spectra of DLE-171 resin (d) after phenol adsorption.

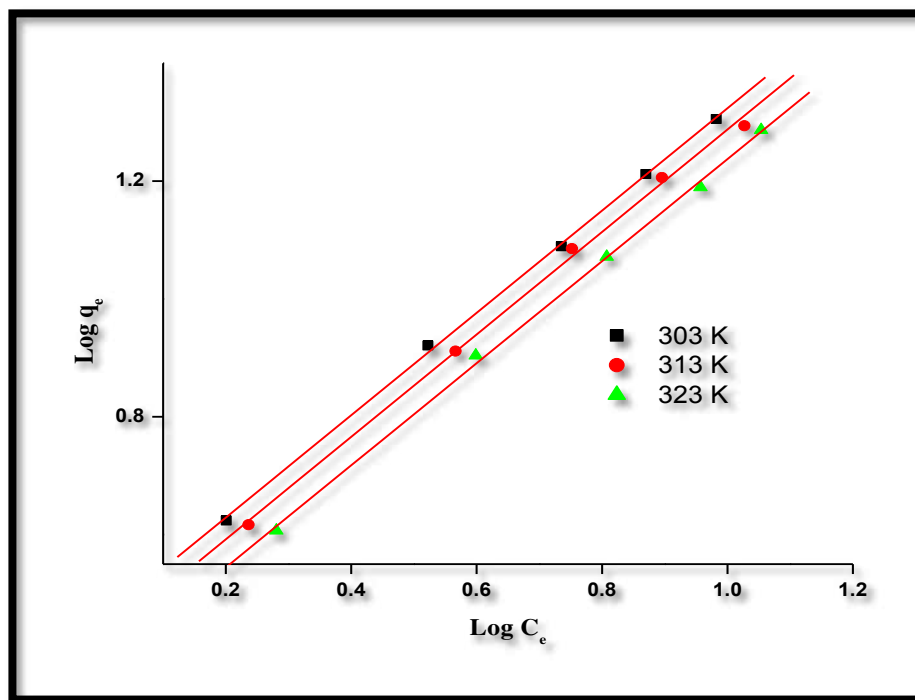


Fig. 8. Freundlich adsorption isotherm of DLE-171 on the removal of phenol.

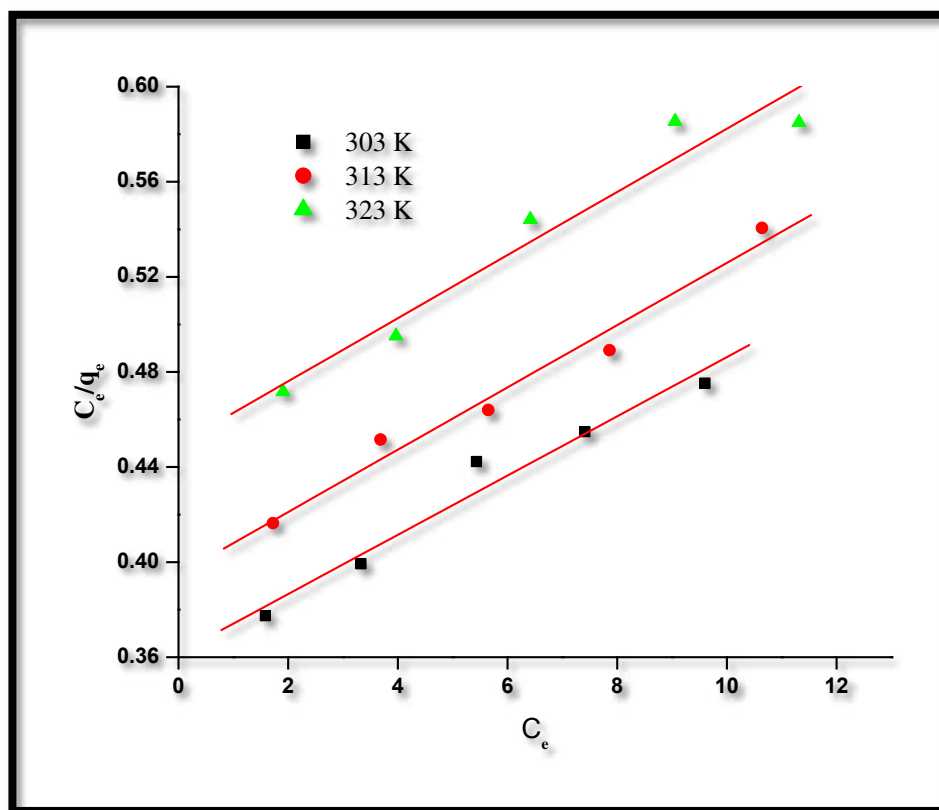


Fig. 9. Langmuir adsorption isotherm of DLE-171 on the removal of phenol.