



Equilibrium, kinetic and thermodynamic studies of removal of phenol from aqueous solution using surface engineered chemistry



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ABSTRACT

Iron impregnated activated carbon has been used as a new adsorbent for the adsorptive removal of phenol from waste water. Impregnation of iron was confirmed by Fourier transform infrared spectroscopy and scanning electron microscope and energy dispersive spectroscopy. Different parameters affecting the adsorption capacity of Iron impregnated activated carbon such as Iron impregnated activated carbon dosage, contact time, pH of solution, initial concentration of phenol and agitation speed were optimized. The residual concentration of phenol was determined by UV-Vis spectroscopy. Maximum adsorption efficiency was calculated 98.5% at optimized parameters: concentration of phenol 25 mg L⁻¹, Iron impregnated activated carbon dose 75 mg, pH 7.0 and agitation time 90 min. The experimental data was fitted to different adsorption isotherms and adsorption capacities obtained were 20 and 15 mg g⁻¹, respectively. Adsorption energy was found to be 1.54 kJ mol⁻¹ which predicts that phenol was adsorbed onto the Iron impregnated activated carbon through physisorption.

1. Introduction

Environmental pollution has been a real problem for the living creatures. It has increased significantly in the past few years and reached to alarming levels in terms of health effects on animals and plants. Ground water pollution has been a serious threat, caused by industrial effluents containing dissolved polycyclic aromatic hydrocarbons (PAHs) and phenols. Phenols are naturally as well as artificially existing compounds. They are found in many industrial effluents, including cooking operations, pharmaceuticals, coal processing, refineries, plastics, wood products, as well as pesticide, paper and paint industries [1, 2]. The US Environmental Protection Agency (EPA) Regulations calls for decreasing phenol content in the effluents to less than 1 mg L⁻¹ [3]. Drinking such contaminated water results in tissue erosion, protein degeneration, and paralysis of the central nervous system and also damages the kidney, liver and pancreas of human body [4]. Water pollution damages the aesthetic nature of water, interference with the process of photosynthesis, destruction of the food web existing in water ecosystem [5].

Therefore, to get the environmental and ecological safety, it is recommended to clean the municipal and industrial wastewater from organic micro pollutants, like phenol to the level excluding their negative

impact on the natural environment and surroundings.

Many techniques have been applied for the remediation of phenol from wastewater, such as electrochemical oxidation [6], adsorption by carbon fibers or activated carbon [7, 8, 9, 10], MWCNT [11, 12, 13], waste materials [14], wet air oxidation [15, 16], chemical coagulation [17], solvent extraction [18], membrane separation [19, 20], bioremediation [21, 22] and photo catalytic degradation [23, 24]. The process of bioremediation has also been used for phenol and low molecular weight (PAHs) but it has shown the limited approach for degradation of (PAHs) due to their high molecular weight [19]. For the mineralization/transformation of these contaminants, another alternate process used is ultraviolet radiation, but it has drawback of being expensive, particularly on large scale [25]. Many alternate techniques (physical and chemical) have been applied for the treatment of phenol contaminated water including venting, using solvents and surfactants. The disadvantage of these techniques is that high concentrations of solvent are required for getting good results [26].

Adsorption is favored by its efficiency and universally applicable [26], for the remediation of organic and inorganic compounds, even at low concentration. Adsorption has advantage of its relative ease of operation both in batch and continuous operation, regeneration and

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reusability of adsorbent [27]. The investigation of effluent treatment containing carboic compounds, have revealed that uptake on activated carbon by adsorption is considered as a most potential treatment technique [28, 29, 30]. The surface properties of activated carbon, i.e. the wide range of porosity and high surface area, ease of separation, cheap operational cost and remarkable adsorption affinity make AC (activated carbon) a versatile and favored material for various applications [31, 32]. The removal of phenol using raw activated carbon is reported by many researchers, while the modified activated carbon for the phenolic compounds remediation is comparatively less reported in the literature [33, 34, 35, 36].

To enhance the efficiency of activated carbon, investigation on the modification and the reusability of AC has been carried out [37]. Therefore, we have focused in our present work on the surface modification of activated carbon to enhance its adsorption affinity towards phenol. The surface was modified by using NaOH followed by the impregnation with iron precursor to get Fe-AC.

2. Experimental

2.1. Equipments

Analysis of phenol was carried out by UV-visible spectrophotometer (Cary 60 UV-Vis, Agilent Technologies), FTIR spectra were recorded by FTIR spectrometer (Perkin Elmer Spectrum BX automatic FTIR spectrometer at 4 cm^{-1} resolution). Shaking was carried out using (Magnetic stirrer, MR Hei – Tec). For pH measurements (Seven Compact pH S210) was used.

2.2. Reagents and solutions

All the chemicals used were of Analytical grade and double distilled water was used. AC was purchased from (Shanxi Sincere Industrial Co, LTD, China, mesh size 12), Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) (Merck), sodium hydroxide (NaOH) (Sigma- Aldrich) were used. Standard solutions of phenol (Merck) were prepared by dissolving appropriate amount in double distilled water. The pH of solutions were maintained using 0.1 M HCl, sodium acetate buffer 3,4,5,6, 0.5 M ammonia and bicarbonate buffer were used.

2.3. Synthesis of adsorbent

The AC was heated for 1 h at 100°C in an oven to get the free moisture AC. For modification, 5g of AC were added in 0.5 M NaOH and mixture was stirred for 30 min at 200 rpm, then the mixture was filtered, washed with distilled water. The activated carbon treated in alkaline solutions shows great affinity the sorption of organic species (like phenol) from aqueous system. Alkaline treated AC was transferred to 1 M $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, and stirred for 6 h for the uptake of iron on the surface of the AC. Finally, the mixture was filtered and washed with distilled water and dried for 6 h in an oven at 110°C .

2.4. Adsorption procedure

The efficiency of modified AC was investigated for the removal of phenol by standard batch procedure. Batch experiments were carried out by taking adsorbent dose (10–200 mg) and concentration of phenol ($10\text{--}100\text{ mg L}^{-1}$) in 20 mL solution and the pH was optimized from 2–10. The solution and adsorbent were allowed to agitate from 10–180 min at 100 rpm for the uptake of phenol ions. All the experiments were carried out at room temperature (25°C). Removal efficiency of FAC surface was calculated using 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 (mg L^{-1}) of phenol respectively. The equation used to determine the phenol amount adsorbed at equilibrium per unit mass of adsorbent (phenol adsorption capacity) is given below:

$$q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

Where q_e is the phenol uptake at equilibrium or adsorption capacity ($\text{mg of phenol g}^{-1}$ of the Sorbent) and V is the volume of phenol solution and m is the amount of Fe-AC.

3. Results and discussion

3.1. Characterization study

The modified AC was characterized by SEM and EDS analysis. EDS is used to determine the elements on sample surface, combined with the observation under SEM. Fig. 1 shows the presence of iron on the surface of AC by SEM and EDS analysis. Fig. 2a shows the spectrum of Fe-AC, an informative peak appeared at 1112.79 cm^{-1} attributed to the presence of iron on the surface.

Fig. 2b confirms the adsorption of phenol on the surface of Fe-AC. The peak at 1566 cm^{-1} indicated the $\text{C}=\text{C}$ aromatic ring stretching vibration [38] while the peak at 685 cm^{-1} is attributed to OH out of the plane bending [39] and confirmed the adsorption of phenol onto the Fe-AC.

3.2. Adsorption studies

3.2.1. Effect of contact time

In order to achieve the maximum uptake of phenol onto Fe-AC, experiments were carried out at variable time intervals from 0 to 180 min. All other parameters were kept constant. The increase in phenol removal efficiency was observed till 90 min where maximum sorption was attained, as shown in Fig. 3. This can be explained from the equilibrium adsorption point at which the rate of adsorption was higher than desorption, at which the optimum sorption was achieved. After 90 min a clear desorption was observed due to the saturation of the active sites on surface of Fe-AC.

The enhanced adsorption of metal with an increase in agitation time may also be due to the decrease in boundary layer resistance in the kinetic energy of the hydrate layer [40]. An increase in adsorption of phenol ions with an increase in contact time may also be due to the decrease in boundary layer resistance of the hydrate layer.

3.2.2. Effect of pH on the phenol removal

The pH of solution has a critical role in the removal of phenol from a water system, because it can affect the charge of adsorbent surface. The removal of phenol by modified AC was evaluated in the pH range from 2–10, while initial concentration of phenol ions, contact time, adsorbent amount, shaking speed were kept constant at 25 mg L^{-1} , 90 min, 75 mg, 200 rpm respectively. The maximum removal efficiency of phenol was recorded at pH 7, as shown in Fig. 4. However, the adsorption of phenol was decreased with the pH greater than 7.

Mechanism can be elaborated on the basis of ionic chemistry of solution and surface charge of Fe-AC. Phenol adsorbs to a lesser extent at higher pH because of its weak acidic nature ($\text{pK}_a = 10$). The repulsive forces between negatively charged surface of AC and phenol may be responsible for the decrease in sorption at higher pH. While up to the pH 7, the electrostatic interaction occurs between the positive ions on the surface and phenolate ions and increases the sorption.

3.2.3. Effect of concentration

The ionic concentration of phenol was optimized from $10\text{--}100\text{ mg L}^{-1}$ to check the removal efficiency on Fe-AC, while all other parameters were kept constant. The maximum uptake of phenol observed was at

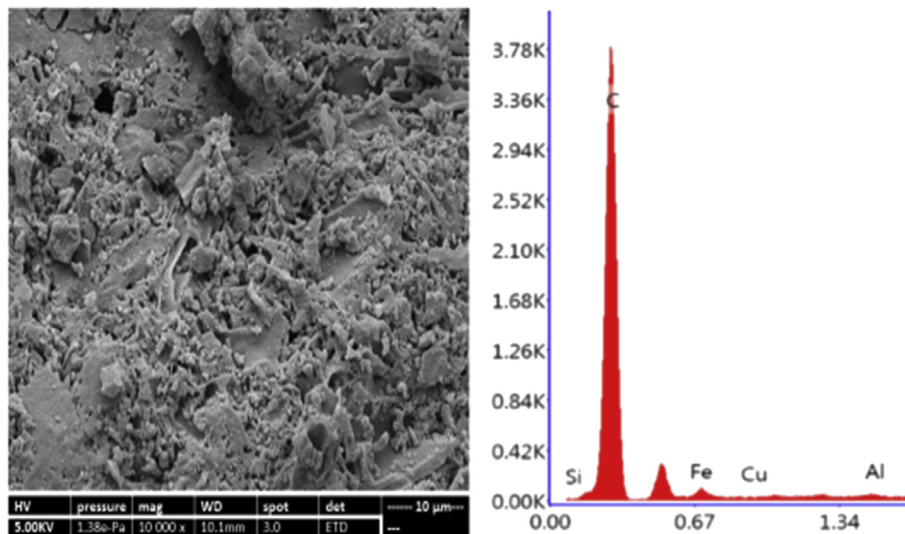


Fig. 1. Scanning electron microscope and energy dispersive spectroscopy images for Fe-AC.

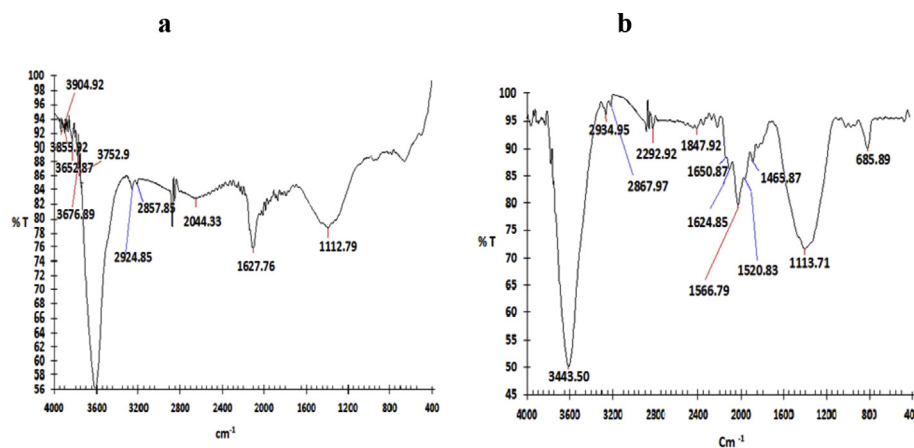


Fig. 2. (a) FTIR spectrum for Fe-AC (b) FTIR spectrum for phenol incorporated on Fe-AC.

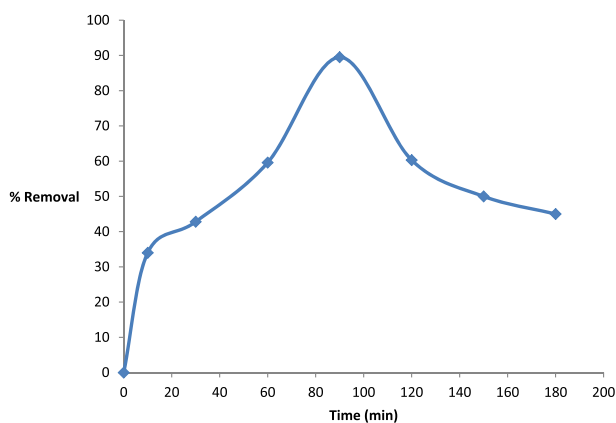


Fig. 3. Effect of shaking time on removal of phenol using Fe-AC at room temperature.

lower concentration shown in Fig. 5, while removal decreased as the initial concentration increased. This can be explained as the high amount of phenol ion with limited active adsorbed sites on the Fe-AC surface, which leading to increase the concentration of phenol ion in the bulk solution and less favourable sites are involved for the uptake of phenol

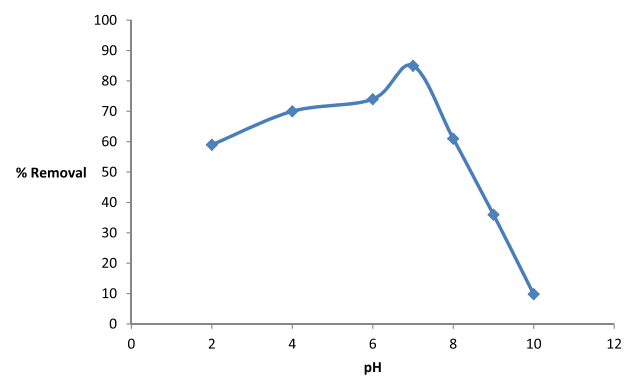


Fig. 4. Effect of pH on the removal of phenol using Fe-AC at room temperature.

ions and thus decreasing the removal capacity. At certain concentration the adsorption sites of Fe-AC surface are equilibrated with the phenol ions, so further increase in the concentration, results in the decrease in uptake on the surface, because all of the sites are occupied.

3.2.4. Effect of adsorbent dosage

The adsorbent is said to be more efficient, if its smaller amount gives maximum uptake of the desired analyte. The effect of the modified AC

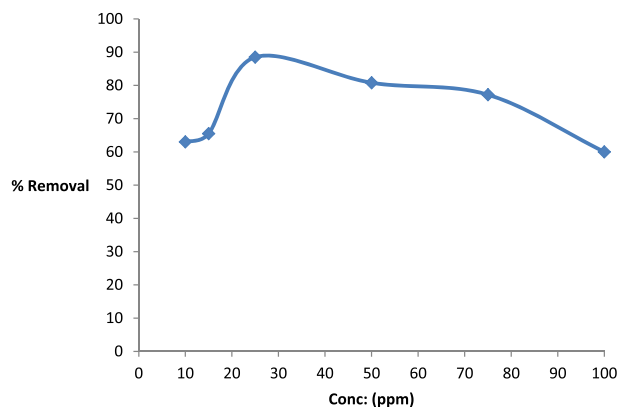


Fig. 5. Effect of conc. on the removal of phenol using Fe-AC at room temperature.

dose was studied from 10–200 mg for the removal of phenol from the water system at pH 7, Concentration 25 mg L⁻¹, shaking time 90 min and at 200 rpm Fig. 6 shows that removal was increased from 10–75 mg due to the increased adsorbent surface area and availability of more vacant surfaced sites. However, slightly decrease in the adsorption was investigated after 75 mg. This reduction in per unit mass of Fe-AC surface can be elaborated on the basis of adsorbent to adsorbate ratio, for the specific solute concentration, adsorption capacity changes depending on the binding sites present on the surface.

At 75 mg of Fe-AC the maximum number of phenol ions occupies the available sites describing the higher per unit mass adsorbent value. However, for more than 75 mg the number of active sites were increased for the same initial concentration of phenol solution, so few active sites on FAC surface remained unoccupied showing the decreased per unit weight sorbent value. Therefore 75 mg was selected optimum dose for the study.

3.2.5. Effect of shaking speed

Shaking provides proper interactions between the molecules in solutions and adsorbent binding sites. Effect of shaking speed on the removal of phenol was studied from 100–300 rpm. Fig. 7 shows that the maximum uptake of phenol ions increased up to 200 rpm, after 200 it seemed constant. This may be due to the rapid transfer of phenol ion towards modifying AC surface with the least opposing force to resist at higher shaking speed. Therefore 200 rpm was selected for subsequent study.

3.2.6. Isotherm study (linear method)

The adsorption of phenol was examined by changing initial concentration of phenol ions from 10–100 mg L⁻¹ using 75 mg Fe-AC/20 mL of phenol solution and 90 min contact time at 200 rpm. The uptake of

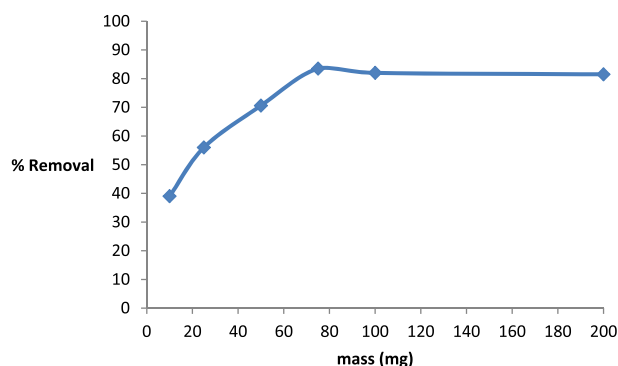


Fig. 6. Effect of adsorbent dose on the removal of phenol using Fe-AC at room temperature.

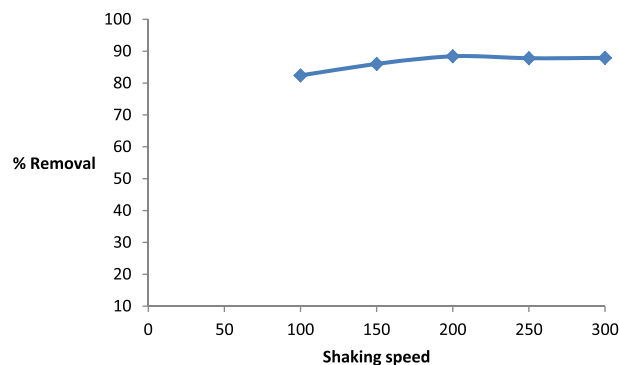


Fig. 7. Effect of shaking speed on the removal of phenol using Fe-AC at room temperature.

phenol ions was maximum at 25 mg L⁻¹. The effect of phenol ions concentration on Fe-AC was also examined in terms of following Eqs. (3), (4), and (5):

$$\text{Langmuir: } \frac{C_e}{C_{ads}} = \frac{1}{Q_b} + \frac{C_e}{Q} \quad (3)$$

$$\text{Freundlich: } \log C_{ads} = \log K_F + \frac{1}{n_F} \log C_e \quad (4)$$

and

$$\text{Dubinin-Radushkevich Isotherms: } \ln C_{ads} = K_D - R - \beta \epsilon^2 \quad (5)$$

where C_{ads} is the quantity of phenol ions captured unit mass of FAC and C_e is the amount of phenol ions in the residual solution at equilibrium. Q , b , A , n , X_m , and β are the Langmuir, Freundlich and D-R constants, respectively [41]. Table 1 shows the all three isotherm constants calculated from their slopes and intercepts of linear plots. Separation factor is the important characteristic of the Langmuir isotherm, determined by using Eq. (6)

$$R_L = 1/(1 + bC_i) \quad (6)$$

where C_i is the concentration of phenol ions before adsorption, monolayer sorption model can be explained by a dimensionless constant R_L [42] to be irreversible ($R_L = 0$), favorable (should lie within 0 and 1), linear ($R_L = 1$) or unfavorable ($R_L > 1$). So, this method presents a favorable sorption for the phenol ions with the R_L values 0.126–0.631. Fig. 8 shows the graphic presentation of Langmuir isotherm. The value of $1/n$ is less than 1, showing that the sorption capacity is only little decreased at lower equilibrium concentrations. The D-R plot was used to calculate the energy for the phenol adsorption system onto Fe-AC using Eq. (7). The energy was found in the range of 1–8 kJ mol⁻¹, which predicts that the uptake of phenol ions onto Fe-AC was physical adsorption [43].

$$E = 1/\sqrt{-2\beta} \quad (7)$$

3.2.7. Non-linear method

Adsorption of phenol onto Fe-AC was also investigated by applying nonlinear form of Langmuir and Freundlich isotherms to determine the sorption parameters and best fit correlation by utilizing the solver add-in with Microsoft Excel. The sorption capacity of Langmuir and Freundlich isotherms were calculated 47.8 mg g⁻¹ and 6.23 mg g⁻¹ respectively. Both the isotherms seemed best fit to the adsorption data with the correlation coefficient were found 0.99 and 0.97 for Langmuir and Freundlich isotherm respectively.

Table 1
Sorption parameters of phenol onto Fe-AC.

Langmuir			Freundlich			D-R		
Q (mg/g)	b (1mol ⁻¹)	r	A (mg/g)	1/n	r	Xm (mg/g)	E (KJ/mol)	r
20	5 × 10 ²	0.994	15	1.021	0.948	8.75	1.543	0.994

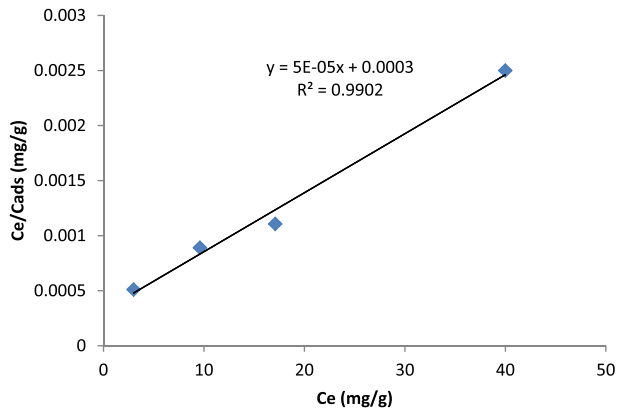


Fig. 8. Langmuir isotherm for the phenol on Fe-AC.

3.3. Kinetics of adsorption

Different kinetic equations like pseudo first order, pseudo second order and Morris–Weber were applied to study the adsorption behavior of phenol on FAC. Intra particle diffusion model was used to study the diffusion mechanism.

3.3.1. Pseudo first order kinetic model

In order to test the validation of data pseudo first order model was applied using following Eq. (8) [44]:

$$\log(q_e - qt) = \log q_e - \frac{kt}{2.303} \quad (8)$$

Where q_e is the quantity of phenol uptake at equilibrium (mg g⁻¹), qt is the quantity of phenol uptake at time t (mg g⁻¹), K_1 is the rate constant (min⁻¹) for the plot of $\log(q_e - qt)$ against t . By plotting the $\log(q_e - qt)$ against t straight line was obtained. The slope and intercept values were used to calculate $\log q_e$ and K_1 for the adsorption of phenol, respectively. The calculated results are shown in Table 2.

3.3.2. Pseudo second order kinetic model

For the equilibrium adsorption pseudo second-order rate equation [45] was applied following Eq. (9):

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (9)$$

Where K_2 (g/mg min) is the second-order rate constant, Slope ($1/q_e$) and intercept ($1/K_2 q_e^2$) were determined from the linear plot of t/qt versus t . Fig. 9 shows best fit between the predicted and original q_e values and comparable to pseudo first order model. Calculated parameters are shown in Table 2.

3.3.3. Moris weber equation

The graph was plotted between the adsorbed phenol concentrations, qt (mol g⁻¹) at time t against $\sqrt{t}$ to check best fitting of Moris Weber equation [8] in the following Eq. (10).

$$qt = k_{pi} \sqrt{t} + C \quad (10)$$

Table 2

Pseudo first, pseudo-second order model, Morris Weber (Intra-particle Diffusion) equation constants and correlation coefficients for adsorption of Phenol on Fe-AC at 25 °C.

Pseudo first order	Pseudo 2nd order	Moris weber
K (min ⁻¹) = 0.008	K (g/mg)min = 0.135	K _{pi} (mg/g min ^{1/2}) = .551
qt (mg/g) = 2.06	qt (mg/g) = 4.7	C = 0.920
r = 0.95	r = 0.98	r = 0.94

Where qt is phenol uptake at time t , k_{pi} is the rate constant of intraparticle diffusion and C is a constant used to estimate the thickness of boundary layer. The thickness of boundary layer can be predicted from intercept value. The higher the intercept value, the greater is the thickness of boundary layer. The plotted graph between the adsorbed concentration of phenol and t results in a straight line which did not proceed through origin, so it can be predicted that intra particle diffusion was not the rate limiting step during the uptake of phenol ions, it may be governed through other mechanisms also involved in the rate determining step [46].

3.3.4. Thermodynamics of adsorption

The uptake of phenol onto the FAC was studied by changing the temperature from 25–50 °C at optimum conditions to evaluate the temperature effect using following Eqs. (11) and (12):

$$\ln Kc = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (11)$$

and

$$\Delta G = -RT \ln Kc \quad (12)$$

Where Kc is the equilibrium constant = $Fe/(1-Fe)$, Fe is the part of phenol ion adsorbed at equilibrium, ΔH , ΔS , ΔG , and T the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively and R is the gas constant.

From the intercept and slope of plots the values of $\Delta H = -5.084889$ kJ mol⁻¹, $\Delta S = 0.00172$ J mol⁻¹K⁻¹ and $\Delta G = -4.50$ to -4.23 kJ mol⁻¹ has been estimated for the phenol ions respectively. The exothermic nature of adsorption was evaluated from inverse value of ΔH , however negative value of ΔG predicted the adsorption process spontaneous and favorable [47].

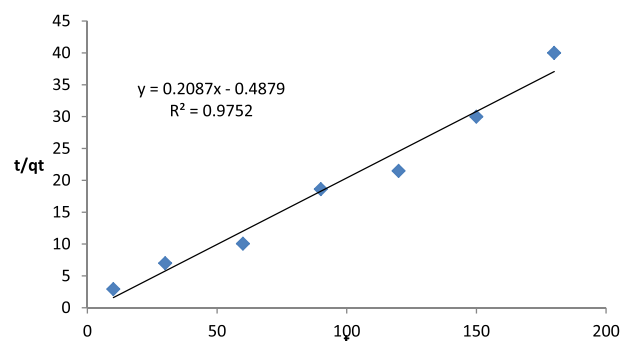


Fig. 9. Pseudo 2nd order plot for the phenol on Fe-AC.

Table 3

Comparison of adsorption capacities of various adsorbents for the phenol.

Adsorbent	Monolayer adsorption	References
	capacity (mg/g)	
MWCNTs	15.9	[46]
PHEMA microbead modified Cibacron blue	8.3	[47]
PHEMA microbead modified alkali blue 6B	13.6	[48]
Samla coal	13.3	[49]
Natural coal	18.8	[50]
Activated coal	1.48	[51]
Activated carbon	1.5106	[52]
AC-TiO ₂	3.153	[52]
Modified Activated Carbon	20	Present work

Table 4

Removal of phenol from real environmental samples.

Samples	Found (mg L ⁻¹)	Added (mg L ⁻¹)	Removal (%)
1*	45	0	97.8
2*	45	10	98.5
3**	0	20	98

Sample 1, 2*: Industrial waste water, Isparta Turkey.

Sample 3**: Tape water, Suleyman Demirel University.

3.4. Comparison with reported methods

The sorption capacity of phenol on modified activated carbon was compared with other adsorbents reported previously are given in Table 3. Adsorption capacity of modified AC is comparable with the most of the adsorbents; whereas the modification of AC is cheaper and simple.

3.5. Method validation

The developed method was applied onto the real spiked samples to check the applicability of current method. The samples were collected from industrial waste water Isparta, Turkey. The removal of phenol from industrial waste water was achieved about 98 % as shown in Table 4. These results are promising performance of Fe-AC for removing phenol from aqueous solution.

4. Conclusions

Modification of AC is simple, economical and effective to treat the water samples containing phenol. Impregnation of iron enhanced the sorption capacity of AC towards the phenolic compounds. Under optimized parameters nearly quantitative adsorption is obtained for phenol on Fe-AC. Results showed that Fe-AC had a rapid rate to reach at equilibrium point with higher uptake ability for phenol. The adsorption isotherms of phenol have been well fitted by all three isotherms namely Langmuir, freundlich and D-R with the correlation coefficient values 0.99, 0.95 and 0.99 respectively. The nature of adsorption was evaluated spontaneous and exothermic reaction was predicted from negative values of Gibbs energy and enthalpy respectively. The second order kinetic model seemed best fit to the adsorption data with the correlation coefficient 0.98. Method was successfully applied for the real environmental samples and it can be concluded that Fe-AC is a new and cheap adsorbent to treat the phenol laden waste water.

Declarations

Author contribution statement

Abdul M. Channa, Sitki Baytak, Saima Q. Memon, Muhammad Y. Talpur: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents,

materials, analysis tools or data; Wrote the paper.

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Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

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