



ISSN: 0976-3376

Available Online at <http://www.journalajst.com>

ASIAN JOURNAL OF
SCIENCE AND TECHNOLOGY

Asian Journal of Science and Technology
Vol. 08, Issue, 10, pp.6165-6172, October, 2017

RESEARCH ARTICLE

STUDY ON REMOVAL OF PHENOL USING ADSORPTION PROCESS

Ashish Kumar, *Vinita Khandegar and Sanigdha Acharya

University School of Chemical Technology, Guru Gobind Singh Indraprastha University,
Dwarka New Delhi-110078, India

ARTICLE INFO

Article History:

Received 22nd July, 2017
Received in revised form
14th August, 2017
Accepted 26th September, 2017
Published online 17th October, 2017

Key words:

Adsorption, Zeolite, phenol,
Isotherms, Kinetics.

ABSTRACT

Wastewaters from various types of industries contain different types of phenols. Phenolic compounds are toxic substances and some are known or suspected carcinogens. Therefore it is important to remove phenol and phenolic compounds from contaminated industrial and aqueous streams before discharged into any water bodies. It is well known that adsorption is an efficient method for removal of various pollutants from wastewater. Several adsorbents have been used for treatment of wastewater and removal of phenolic compounds. In the present study, efforts have been made for removal of phenol from aqueous solution using zeolite as an adsorbent. The adsorbent potential was tested on batch synthetic solutions containing 1-5 (mg/L) phenol concentration at room temperature. The influence of solution pH, adsorbent dose, contact time and initial phenol concentration on the removal efficiency of phenol from water was investigated. A 94 % phenol removal efficiency was obtained for an adsorption time of 4 hr at 7 pH and 1 g of adsorbent dose. The experimental data were modeled using the Langmuir, Freundlich isotherms. The Langmuir model was found to best represent our data revealing a monolayer adsorption with a maximum adsorption capacity 1.19 mg/g at 25 °C, for 1 g of adsorbent dose and 5 mg/L initial phenol concentration. The kinetic data were analyzed using pseudo-first-order, pseudo-second-order and intraparticle diffusion model. The results suggested that the phenol adsorption at room temperature was best represented by the pseudo-second-order equation. The study showed that the zeolite can be used as ecofriendly and effective sorbent for the removal of phenol from aqueous solutions.

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INTRODUCTION

Phenol (hydroxybenzene) is a colourless, crystalline substance of characteristic odour, soluble in water and organic solvents. The monohydroxy derivative of benzene is known as phenol. Phenol is recovered from coal tar from petrochemical industry. It is a colourless or white solid when it is pure. The odour threshold for phenol is 0.04 ppm, with a strong very sweet odour. It is very soluble in water and quite flammable. Phenol was one of the first compounds inscribed into the list of Priority Pollutants by the US Environmental Protection Agency (US EPA, 1987). It penetrates the environment through vehicle exhaust, and it is used as a disinfectant and reagent in chemical analysis. Phenol is also formed as the result of chemical reactions that occurred in the atmosphere in condensed water vapour that forms clouds. Phenol and phenolic compounds are organic pollutants and also found in many industrial effluents such as synthetic resins, plywood

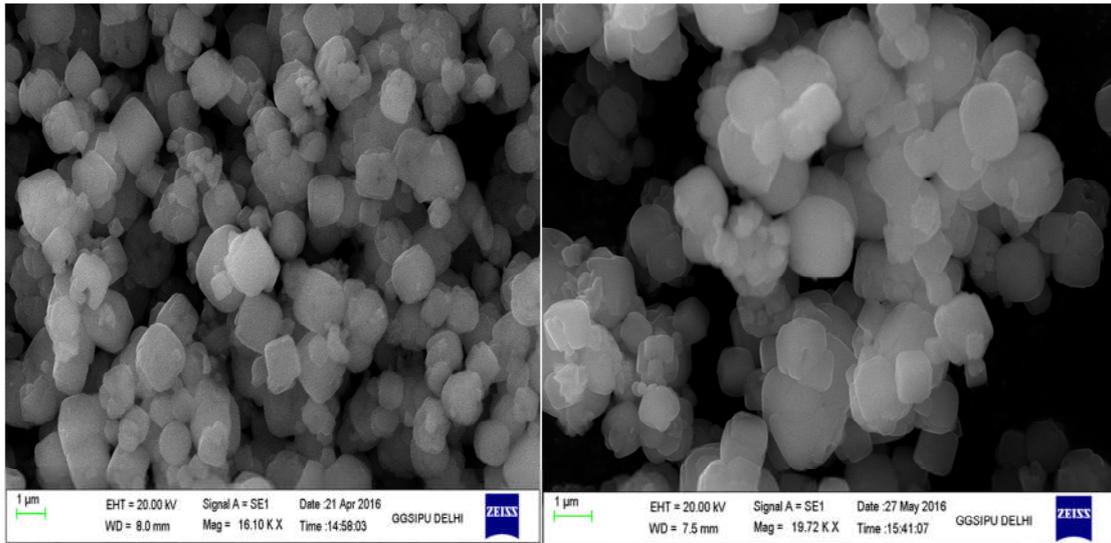
industries, paper and pulp, gas and coke oven plants, paints, coal gas, tanning, textile, plastic, rubber, pharmaceutical, petroleum and mine discharges. Relative fast degradation of phenol causes its concentration in waters exposed to strong anthropogenic pollution (Michałowicz and Duda 2007). The health hazards caused by phenol are given in Table 1. Spiridon *et al.*, (2013), reported that phenol and its derivatives are among the most frequently used organic compounds. They are the basis of the synthesis of many different products such as phenolic and epoxy resins, adhesives, pharmaceuticals, insecticides, pesticides, etc.

On the other hand, phenolic compounds are important contaminants of the wastewater generated by various phenol based technological processes: oil extraction and refining, coal conversion, textile and leather industry, plastics industry, paint manufacturing, olive oil production, etc. (Hameed and Rahman 2008; Polat *et al.*, 2006; Hamdaoui and Naffrechoux 2007; Kennedy *et al.*, 2007; Lin *et al.*, 2009; Lu *et al.*, 2011). Therefore, the major source of phenols are municipal and industrial sewage, in natural waters and in some situations even in drinking water also. When drinking water is chlorinated, phenol, if present, is easily transformed into chlorophenols, compounds even more toxic than phenol.

*Corresponding author: Vinita Khandegar,
University School of Chemical Technology, Guru Gobind Singh
Indraprastha University, Dwarka New Delhi-110078, India.

Table 1. Health hazards caused by phenol

Mode of Exposure	Effect on health
Inhalation	<ul style="list-style-type: none"> • Can irritate the nose, throat, and lungs • Higher exposures may cause a build-up of fluid in the lungs.
Oral, Eyes, Skin	<ul style="list-style-type: none"> • Ingestion of as little as 1 gram can be fatal to humans. Can also cause severe eye damage, including blindness. Irritating and corrosive to the skin <ul style="list-style-type: none"> • Little or no pain may be felt on initial contact due to its local anaesthetic effect. • Skin contact will cause the skin to turn white; later severe burns may develop.
Chronic exposure	<ul style="list-style-type: none"> • Rapidly absorbed through the skin; toxic or fatal amounts can be absorbed through relatively small areas. • Repeated or prolonged exposure to phenol or its vapours may cause headache, nausea, dizziness, difficulty swallowing, diarrhoea or vomiting. • Can affect the central nervous system, liver and kidneys.



(a) (b)

Fig. 1. SEM Images (a) zeolite (b) phenol loaded zeolite

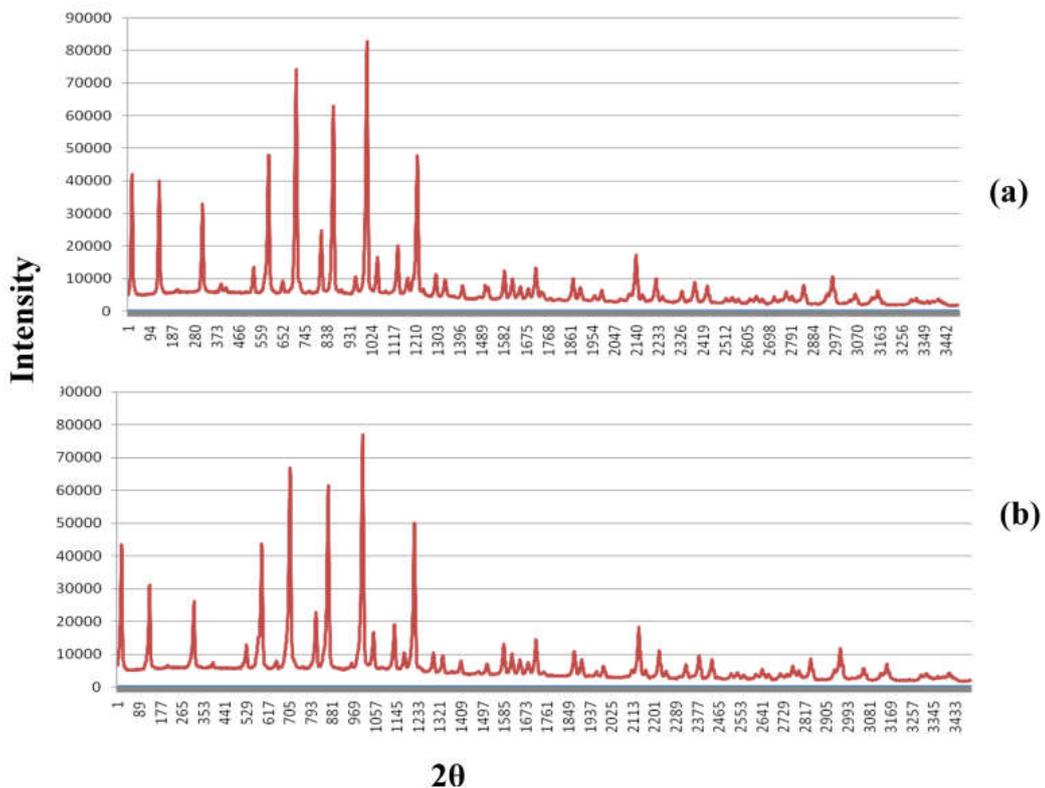


Fig. 2. XRD Images (a) zeolite (b) phenol loaded zeolite

The presence of these compounds generates an unpleasant odor and water taste (Yousef and El-Eswed 2009). Due to its high toxicity, solubility and low biodegradability, phenol is considered one of the most dangerous water contaminants having a high carcinogenic potential (Ming *et al.*, 2006; Zhang *et al.*, 2009). Different studies have shown that phenol and its derivatives cause undesirable and harmful effects on animals and humans even at concentrations lower than 0.1 ppm (Saravanakumar and Kumar 2011). The usage of phenol contaminated drinking water affects the central nervous system, the cardiovascular and urogenital systems, also causing degeneration of proteins and erosion of tissues in the body. These medical conditions cause damage to the kidneys, liver and the pancreas. The side effects are various: convulsions, coma, cardiac disorders, respiratory failure and, at prolonged exposures, collapse (Hameed and Rahman 2008; Lin *et al.*, 2009). The discharge limit of phenol is 0.1mg/l and 0.001mg/l by world health organization and environmental protection act respectively (WHO 1993; USEPA 1987). Therefore, phenol is taking as a priority pollutant. Discharge of phenol from various industries has been summarized in Table 2.

Table 2. Phenol in various industrial effluents (Metcalf & Eddy, Inc 2003; Busca *et al.*, 2008)

Industry	Phenol concentration (mg/L)
Refineries	40-185
Coal processing	9-6800
Coking	28-3900
Petrochemicals manufacturing	200-1220
Textile	100 - 150
Leather	4.4 - 5.5
Coal conversion	1700 - 7000
Ferrous industry	5.6 - 9.1
Rubber industry	3 - 10
Pulp and paper	22
Wood preserving	50 - 953
Phenolic resin production	1600
Fiberglass manufacturing	40 - 2564
Paint manufacturing	1.1

A number of methods such as biological treatment (Lu *et al.*, 2011; Bajaj *et al.*, 2008; Moussavi *et al.*, 2010), coagulation and electrocoagulation (Bazrafshan *et al.*, 2015; Bazrafshan *et al.*, 2016), ultrasonic degradation (Mahvi 2009; Maleki *et al.*, 2007; Pandit *et al.*, 2001), activated carbon adsorption and other adsorbents (Zarei *et al.*, 2013; Mahvi *et al.*, 2004; El-Naas *et al.*, 2010; Dursun *et al.*, 2005; Gurses and Yalcin 2005), membrane filtration (Bodalo *et al.*, 2009), enzymatic treatments (Mao *et al.*, 2006), solvent extraction (Juang *et al.*, 2010), photocatalytic degradation (Mahvi *et al.*, 2007), chemical oxidation and electrochemical methods (Canizares *et al.*, 2002; Tahar and Savall 2009; Yavuz and Kopal 2006), are the most widely used methods for removing phenol and phenolic compounds from wastewaters. These methods have been found to be limited, since they often involve high capital and operational costs. On the other hand ion exchange and reverse osmosis are more attractive processes because the pollutant values can be recovered along with their removal from the effluents. Reverse osmosis, ion exchange and advanced oxidation processes do not seem to be economically feasible because of their relatively high investment and operational cost (Khandegar and Saroha 2013; Nazari *et al.*, 2007). Efficient techniques for the removal of highly toxic organic compounds (phenol) from water have drawn significant interest. Among the possible techniques for water

treatments, the adsorption process shows potential as one of the most efficient methods for the treatment and removal of phenolic compounds from wastewater. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required. The adsorption process is widely used for treatment of industrial wastewater. In the present work, application of zeolite is investigated for removal of phenol from synthetic solution.

MATERIALS AND METHODS

All analytical grade chemicals were commercially used without any further purification. Phenol (purity 99.8%, Sigma Aldrich), Deionized water (H₂O, home-made), zeolite (Qualigens, India). Sodium hydroxide (Merck, India) and sulphuric acid (Merck, India) were used to adjust the pH of the initial solution. Synthetic stock solution of phenol (100 mg/L) was prepared and solutions of lower concentration were made by dilution of stock solution with distilled water. The batch kinetic adsorption study was conducted at room temperature (25°C). A 250 ml of phenol solution was taken in 300 ml flask. A known amount (1 g) zeolite was added in flask containing phenol (concentration 1-5 mg/L) and agitated in a incubator shaker at 150 rpm for different contact time. After each experiment, the content from flask was taken separately and filtered. The residual concentration of filtrate was analyzed by standard APHA method UV-VIS spectrophotometer (Hitachi UV-2900) at wavelength 270 nm against blank. The phenol removal efficiency (PRE) was calculated using equation (1). All experiments were carried out in duplicate and the concentration of phenol retained in the sorbent phase (q_e, mg/g) was calculated using equation (2).

$$C_E = \left(\frac{C_o - C_i}{C_o} \right) \times 100 \quad (1)$$

$$q_e = \left[\frac{(C_o - C_e)}{m} \right] \times V \quad (2)$$

where PRE = adsorption percentage (%)

C_o = Initial concentrations of phenol (mg/L)

C_i = Final concentrations of phenol (mg/L)

C_e = Equilibrium concentrations of phenol (mg/L)

Q_e = Equilibrium adsorption capacity (mg/g)

m = adsorbent dosage (g)

V = Volume of solution (L).

Zeolite characterization

Scanning Electron Microscopic Analysis (SEM) is one of the mostly used characterization technique applied for studying the surface morphology, properties, porosity and texture of the adsorbent. In the present study, the surface morphology of raw zeolite and phenol loaded zeolite after treatment of phenol containing solution were investigated. SEM analysis was carried out at room temperature by SEM-ZEISS-50 operated at 20 kV accelerated voltage and magnification of 16KX and 19KX. The crystalline structure of zeolite was determined by X-ray diffraction (XRD) analysis using (XRD - Philips Expert 1), with CuKα radiations of wavelength (λ = 1.5406 Å), generated at 30 Kv-30 mA. The scan measurements were

performed at 2θ range of $0-1025^\circ$ with a scanspeed of $4^\circ/\text{min}$ in sampling pitch of 0.02° .

Adsorption Isotherms

Equilibrium equation, commonly known as adsorption isotherm. For design of a adsorption system the isotherm study is a basic requirement. The isotherm provides information on the capacity of the sorbent or the amount required for removing a unit mass of pollutant under the operating conditions. For design of adsorption system, Langmuir, Freundlich isotherms were tested in the present study.

Adsorption kinetics

Equilibrium study is important for determining the efficiency of adsorption process. It is also necessary to identify the adsorption mechanism for a given system. Kinetic models have been exploited to test the experimental data. Also to find the mechanism of adsorption and its potential rate controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of phenol is required to select the optimum conditions for removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid-solution interface. Several kinetic models are used to explain the mechanism of adsorption processes. In the present work, kinetic studies were carried out at constant pH 7 with an initial concentration of (1-5 mg/L) and adsorbent dose of 1g/L at room temperatures using pseudo-first-order, pseudo-second-order and intraparticle diffusion model.

RESULTS AND DISCUSSION

The SEM images of raw zeolite and phenol loaded zeolite were recorded and shown in Fig. 1 (a) and Fig. 1 (b). It was found that, the zeolite consist of many sphere-like domains, with relatively uniform sizes of 1-2 μm , which are macrostructures. In Figure 1(a), the bright spots show the rough and porous surface of the adsorbent, which is one of the factors increasing adsorption capacity. The phenol loaded SEM images Figure 1(b) shows the adsorption of phenol on the zeolite and depicting the surface of phenol particles after adsorption, it is clearly seen that the sides of zeolite particle, pores and surfaces were covered by phenol and become large sphere. It is evident that the structure of zeolite has changed after adsorbing the phenol from the solution. The XRD patterns of zeolite and phenol loaded zeolite are very similar and indicating that the crystalline nature. The XRD results of raw zeolite and phenol loaded zeolite are shown in Fig. 2(a) and Fig. 2(b) respectively. The sharp diffraction lines at 1° and 1000° were observed in the both the samples. This pattern confirms the zeolite has mesoporous structure of the pores.

Effect of pH of the solution

Experiments were conducted at different pH [3 to 9] to study the effect of pH on removal efficiency and the results are shown in Fig. 3. The pH of the working solutions was adjusted using NaOH or H_2SO_4 Solutions. Experiments were conducted at room temperature and the initial concentration of phenol was 1 to 5 mg/L, 1 g of adsorbent and 2 hr of contact time. It can be noticed from the Figure 3 that the phenol adsorption has a relatively similar trend for each of the considered initial

concentration the results are in good agreement with other published data (Agarry *et al.*, 2013; Spiridon *et al.*, 2013; Agarry and Ogunleye 2015). It can be seen that removal efficiency significantly increases from pH range 4 to 7 and declines with pH above 7. Within the middle part, between 4 and 7, pH does not bring less significant changes of the phenol uptake by Zeolite. The possible reason for that trend is phenol-zeolite interactions (Yousefand El-Eswed 2009). It is well known that phenol is a weak acid with pKa of 9.9. At pH under this value, the protonated, neutral form is predominant. The rise of pH determines the increase of the concentration of deprotonated form. Koubaissy and coworkers (2011) reported that the phenol adsorption on zeolite considers a complex donor acceptor mechanism and this behavior clearly reduces the phenol adsorption. For a pH range from 4 to 7, the concentration of protons diminishes and phenol is present in its neutral form, being thus easily adsorbed onto zeolite. At pH above 7 phenol adsorption would be reduced due to repulsions between its predominant anionic form and adsorbent surface.

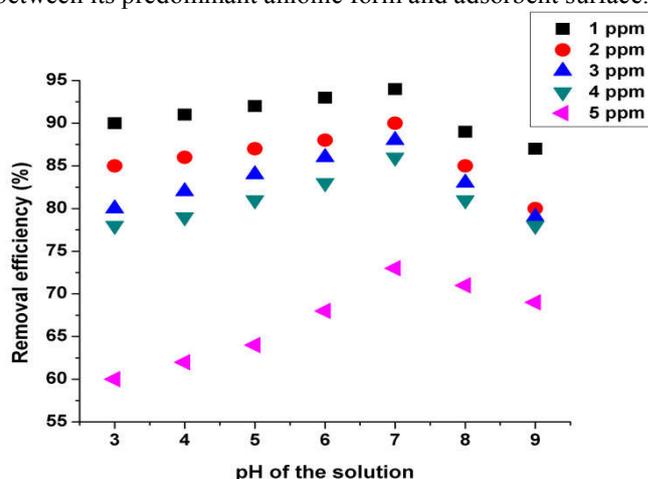


Fig. 3. Effect of Solution pH: (Time= 4 hr, agitation speed = 150 rpm, dose= 1 g m)

Effect of contact time

Experiments have been conducted for phenol removal by varying contact time from 1 hr to 6 hr and the results are shown in Fig. 4. Figure 4 depicts the effect of contact time on the removal of phenol at various initial concentrations (1 to 5 mg/L). It can be observed from the Figure 4 that the phenol removal efficiency increases significantly (50% - 94.2%). After 4 hr the removal efficiency was nearly constant around 94 %. The results are in agreement with those reported in the literature (Saravanakumar and Kumar 2011). It can also noticed from Figure 4 that the saturation curve rise sharply in the initial stages, the phenol adsorption rate is high at the beginning of the experiment because initially the adsorption sites are more available and phenol ions are easily adsorbed on these zeolite sites. Eventually, a plateau is reached in all curves indicating that the adsorbent is saturated at this level. It was found that the contact time needed for removal of phenol from the solutions is 4 hr. However, for phenol solutions with higher initial concentrations, longer equilibrium times will required. It was also seen that an increase in initial phenol concentration resulted in increase the phenol uptake. The removal curves are single, smooth and continuous, indicating the formation of monolayer coverage of the phenol molecules onto the outer surface of the zeolite.

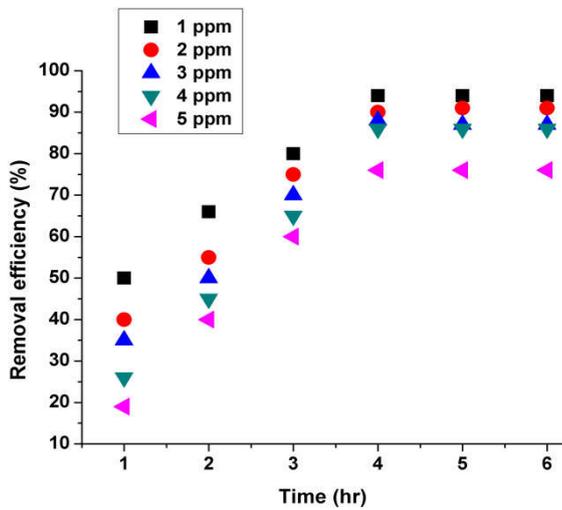


Fig. 4. Effect of Contact time (pH of the solution =7, agitation speed =150 rpm, dose 1 gm)

Effect of adsorbent dose

The effect of zeolite amount on phenol removal efficiency was investigated in the range from 1 to 3 g at different initial concentrations of phenol (1 to 5 mg/L). Experiments were conducted at the ambient temperature, 4 hr adsorption time, 150 rpm shaking speed and at 7 pH. The results are presented in Fig. 5. It can be noticed from Fig. 5 that the phenol removal efficiency increases with increase in zeolite dose (1 to 3 g). This may be attributed to the increase in adsorbent dose leads to increase the adsorbent surface area, pores, active sites and the number of unsaturated sites (Ali *et al.*, 2016). This will have a greater accessibility to the zeolite surface, which would lead to a higher extent in the adsorption process. In the present study, 1 g of zeolite is considered as the optimum dose. Similar type of findings has been reported in the literature (Saravanakumar and Kumar 2012).

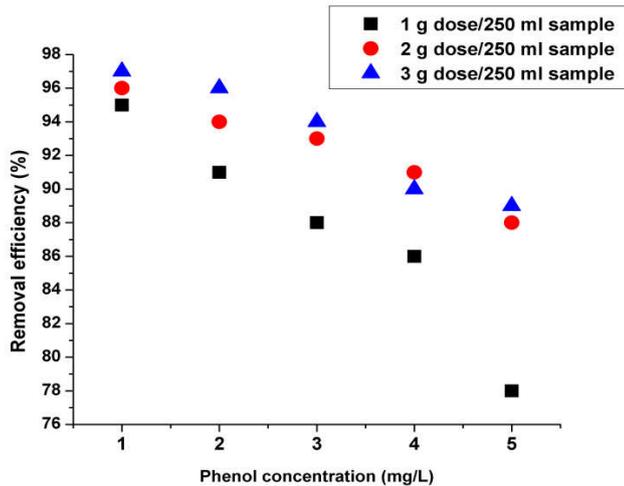


Fig. 5. Effect of adsorbent dose (pH of the solution =7, Time= 4 hr, agitation speed = 150 rpm)

Adsorption isotherm models

Adsorption equilibrium is a fundamental property in adsorption studies. In order to optimize the design of an adsorption system for phenol removal from aqueous solution, it is important to find the most appropriate correlation for the

equilibrium curve. Adsorption isotherm models are described in many mathematical forms, some of which are based on a simplified physical description while others are purely empirical and intended to correlate experimental data. Fig. 6 (a) and Fig. 6 (b) shows the Langmuir and Freundlich isotherm models to the experimental equilibrium data in order to verify which model presented the best adjustment. The Langmuir, Freundlich isotherm model and separation factor (R_L) determined using equation (3 to 5) (Langmuir 1918; Freundlich and Helle 1939).

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b} \tag{3}$$

$$\log q_e = \frac{1}{n_f} \log C_e + \log K_f \tag{4}$$

$$R_L = \frac{1}{1 + bC_0} \tag{5}$$

Where C_e is the equilibrium concentration of phenol in the solution (mg/L),

q_e is the equilibrium uptake of phenol on the adsorbent (mg/g),
 q_m is the maximum adsorption capacity (mg/g),
 b is the Langmuir constant (L/mg),
 n is the adsorption intensity
 K_f is the adsorption capacity,

The isotherm parameters for different concentration (1 to 5 mg/L) of phenol are listed in Table 3. R_L value provides significant evidence about the adsorption nature. Langmuir isotherm is considered irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$), unfavorable ($R_L > 1$). The values of n_f in the range 2-10 represent good, 1-2 moderately difficult, and less than 1 poor adsorption characteristics. It can be noticed from Table 3 that the Langmuir model was found to best and revealing a monolayer adsorption with a maximum adsorption capacity (1.19 mg/g), R^2 (0.989) at 25 °C, for 1 g of adsorbent dose and 5 mg/L initial phenol concentration. The separation factor (R_L) and sorption intensity (n) indicates a favorable adsorption.

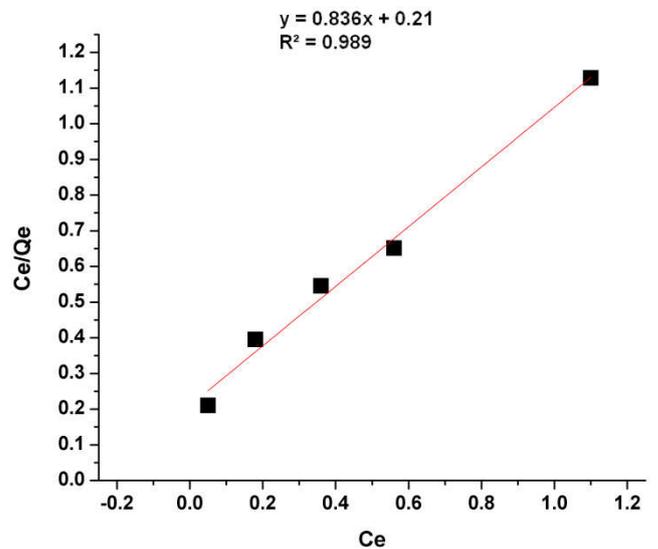


Fig. 6 (a). Langmuir plot

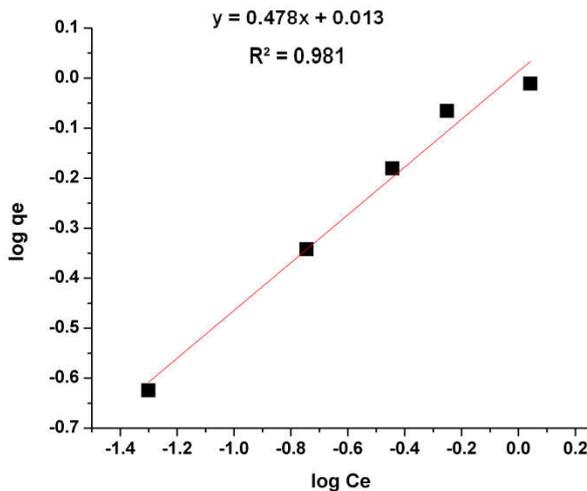


Fig. 6 (b). Freundlich plot

Table 3. Langmuir and Freundlich isotherm model

Adsorption Model	Parameters	Values
Langmuir Isotherm	q_m (mg/g)	1.196
	b (l/mg)	3.98
	R_L	0.2 to 0.04
	R^2	0.989
Freundlich Isotherm	K_F ((mg/g)/(mg/L) ^{1/n})	1.031
	n	2.09
	R^2	0.981

Kinetics of the adsorption

In the present study, the rate controlling step determined by study adsorption kinetics. The kinetics of adsorption processes have been analyzed by the Pseudo-first-order model, Pseudo second-order model and intraparticle model. The pseudo-first-order kinetic model equation describes the rate of adsorption is directly proportional to the number of unoccupied sites by the solutes and is generally expressed by equation (6) (Lagergren and Svenska, 1898). Pseudo-second-order equation describes the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Dada *et al.*, 2012). The pseudo-second-order equation can be expressed using equation (7). Intraparticle diffusion plays a significant role in controlling the kinetics of the adsorption process. The intraparticle model can be expressed by equation (8).

$$\log(q_e - q_t) = \log q_e - (K_1/2.303)t \quad (6)$$

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

$$q_t = k_p t^{1/2} + C \quad (8)$$

Where q_e is the amounts of phenol adsorbed (mg/g) at equilibrium.

q_t is the amounts of phenol adsorbed (mg/g) at time t (min)

k_1 is the pseudo-first-order rate constant (L/min).

k_2 is the pseudo-second-order rate constant (g/ mg min)

k_p is the intra-particle diffusion rate constant (mg/g min).

All kinetic parameters are summarized in Table 4. It can be noticed from Table 4 that the pseudo second-order kinetic model was good fitted the kinetic data as compare to the pseudo first-order kinetic model. this model assumes that, the rate-controlling step is chemisorptions involving valency forces through sharing or exchanging of electrons between adsorbent and adsorbate.

Table 4. Kinetic model

Kinetic model	Parameters	Values
Pseudo first order	K_1 (1/min)	0.248
	R^2	0.985
Pseudo second order	K_2 (g/mg.min)	2.34
	q_e (mg/g)	0.29
	R^2	0.988
Intra-particle diffusion	K_P (mg/g min ^{0.5})	0.082
	C	0.301
	R^2	0.923

Conclusions

Chemical contamination of water from a wide range of toxic pollutants, especially aromatic molecules, is a serious environmental problem due to potential human and environmental toxicity. Phenol and its derivatives appear to be the major organic pollutants globally in this century. They derived from many chemical plants, pesticide and dye manufacturing industries. This derivatives cause serious threat to human health and to natural water. Adsorption is relatively new practice for the removal of phenol and its derivatives. In the present work points out that zeolite proves to have a significant potential for removal of phenol from wastewater. Based on the experimental results of this study, the following points can be concluded:

- In this study, phenol from aqueous solution was investigated using zeolite as an adsorbent and it was found that the adsorption clearly depends on contact time, adsorbent dose, pH, and phenol concentration.
- The R^2 value of Langmuir isotherm model was the highest as compare to Freundlich isotherm model. The maximum monolayer coverage (q_m) from Langmuir isotherm model was determined to be 1.196 (mg/g) and the separation factor (R_L) indicating a favourable adsorption experiment. Also from Freundlich isotherm model, the sorption intensity (n) indicates favourable sorption.
- It was found that the pseudo second-order kinetic model was good fitted the kinetic data as compare to the pseudo first-order kinetic model. This model assumes that, the rate-controlling step may be chemisorptions involving valency forces through sharing or exchanging of electrons between adsorbent and adsorbate.

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