

Adsorption of phenol from aqueous solution by modified zeolite with FeCl₃

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INTRODUCTION

Phenol is one of the most significant compounds in industrial wastewater. According to the report of American Institute of

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ABSTRACT

Aims: The objective of this study was to evaluate phenol removal from a synthetic solution using modified zeolite (clinoptilolite) with FeCl₃ as an adsorbent.

Materials and Methods: The zeolite samples were crushed and granulated using standard ASTM sieves (mesh size of 20). The prepared zeolite then was modified by FeCl₃. The chemical composition and the surface area of the zeolite were analyzed using XRF and N₂ gas via BET isotherm and Belsorb software. In this study, different parameters including pH (3, 7, and 12), initial concentration of phenol (25-200 mg/l), contact time (20-240 min) and the amount of modified zeolite (0.25-3 g/l) were examined in a batch reactor. The concentration of phenol was measured at wavelength of 500 nm by a spectrophotometer.

Results: The results of this study showed that as the initial concentration of phenol, the adsorbent dose and the pH in the range of 3-12 increased the adsorption / removal of phenol increased. Phenol adsorption equilibrium was achieved within 100 min contact time and the optimum pH for adsorption of phenol using zeolite was found as 3. The adsorption data complied with Langmuir isotherm ($r^2=0.98$).

Conclusions: The results showed that modified zeolite can be used effectively in removing phenol. The removal efficiency of phenol in lower pH was more than in higher pH. Also, due to the low price of the zeolite and its simple modification, it can be used for removing hazardous pollutants in water and wastewater.

Key words: Adsorption, clinoptilolite, modified zeolite, phenol

Chemical Sales, global phenol production capacity was 8.4 million tons in 2004. Phenol is a raw material in different industries of petro chemistry, pharmacy, plastics, and chemical pesticides^[1] and is largely found in industrial wastewater of coal refineries, resin and paint industries, fungicide and herbicide production, textile, and pulp industries.^[2,3] Phenol is a known environmental pollutant, since it is quite toxic^[4-6] and is lethal at low concentration (5-25 mg / l) for the fish, and causes the unpleasant taste in drinking water at the concentration of around 0.5 mg/l. It was included in priority pollutants list by American Environmental Protection Agency (US-EPA) whose level in drinking water was determined

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less than 0.5 $\mu\text{g}/\text{l}$. The industries which produce or use this chemical often generate wastewater contaminated by substantial amounts of phenol (0.1-10% by weight).^[1,7,8] Moreover, the influx of phenol into the drinking water disinfected by chlorine compounds causes the formation of chlorophenol compounds making important environmental and health problems. These compounds make the taste and odor of the water unpleasant and inappropriate for consumption.^[2,9,10] Therefore, treatment of wastewater containing phenol by appropriate methods is essential before it discharges to the environment in order to prevent environmental and health hazards. Methods presented in scientific literatures for removing phenol are classified into three major categories: physical, biological, and chemical methods like adsorption, advanced oxidation, wet and chemical oxidation, and biological processes. The adsorption process using activated carbon is a method for phenol removal. Generally, adsorption is a process of collecting materials that are dissolved in a suitable interface. Various materials which are used in adsorption include powder and granular activated carbon, ash, bentonite, hydrated cellulose phosphate, biomass, powder activated coal, coke coal, kaolin; of which the activated carbon is among the most effective materials in this regard. The high cost of activated carbon regeneration caused the researchers to use new adsorbents.^[11-14] In this respect, numerous studies have been conducted on the adsorbents, which are used easily and are cost-effective. Today, the use of zeolite in pollutants removal has been studied and considered due to its low cost, naturalness, accessibility, and eco-friendliness.^[15] Zeolites are crystalline hydrated aluminosilicate having alkali and alkaline-earth metal cations and an infinite structure. One of their properties is cation exchange and reversibility of water adsorption and desorption without causing main changes in molecular structure. Natural zeolite normally has negative electric charge on its surface and thus, it has the only feature of ion exchange.^[16] In recent studies, the impregnation process was used to increase the efficiency of these compounds in removing pollutants from the environment. Covering the adsorbents with various metal compounds (ionic and elemental) is a method to improve pollutants removal by adsorption media. Varieties of trivalent iron oxides have been studied due to their high affinity to remove pollutants.^[17] In this study, clinoptilolite was modified by FeCl_3 and tested as an adsorbent for phenol removal due to its high selectivity property, high cation-exchange capacity, resistance to environmental conditions, and frequency.^[12,15]

MATERIALS AND METHODS

The used zeolite supplied by mines in Semnan, Iran. It was crushed and granulated using standard ASTM sieves with mesh size of 20 to achieve small particles (0.85 mm).^[18] The samples were rinsed with distilled water several times and dried off, and placed into the oven in 1% HCl solution for 24 hours. In the next stage, the samples were rinsed with distilled

water and placed into the oven at a drying temperature of 105°C for 14 hours. Then, the samples were put into the 0.1 M FeCl_3 solution. After that, the mixture was shaken for 72 hours and then dried at 105°C for 24 hours. Finally, the mixture was rinsed with distilled water and kept at 100°C for 14 hours.^[19-21] One of the important features of any adsorbent is the pH of point of zero charge (pH_{PZC}).^[22] To determine pH_{PZC} , 0.01 M NaCl solution was used as an electrolyte and 0.1 M HCl and NaOH solutions were used as controlling factors. The amount of 30 ml of the electrolytic solution was poured into each 50 ml Erlenmeyer flask (8 flasks) and the pH of the flasks was adjusted using HCl and NaOH solutions into the range of 2-12. The amount of 0.5 g of zeolite was added to the each flask. The flasks were placed on a shaker with the speed of 120 rpm for 48 hours. Then, the final pH of the flasks after filtration was determined using a pH meter (model Sense Ion 375). The pH_{PZC} was specified after drawing a curve for pH shifts versus initial pH.

The chemical composition of zeolite was analyzed using X-ray diffraction (XRF of Philips Co.). The specific surface of modified zeolite was measured using N_2 gas via Brunauer-Emmett-Teller (BET) isotherm and the calculations was done using the 5th version of Belsorb software. To do the experiments, 1000 mg/l of phenol stock solution was prepared by adding 1 g of phenol to the distilled water. Then, the standard curve for measurement of phenol concentration in the standard and unknown samples was drawn using a UV/VIS spectrophotometer (Japan, Shimadzo - 1700) and a calibration curve was drawn at wavelength of 500 nm.^[23] In this study, the effects of different parameters including contact time, initial concentration of phenol, pH of the solution, and the adsorbent dose were examined and ultimately, the adsorption isotherms were determined.

In order to evaluate the effects of pH and contact time, samples with initial pH of 3, 7, and 12 with a fixed concentration of phenol (100 mg/l), and adsorbent dose of 1 g were prepared and placed into an orbital shaker (model GFL 3017) with the speed of 150 rpm at constant temperature of 20-25°C for 240 minutes. Then, the phenol residue of the samples was measured and the amount of adsorbed phenol was determined per unit mass of adsorbent. In addition, a blank sample was used in each stage of in this study. The volume of the samples was 250 ml in all experiments. To evaluate the effect of phenol concentration in adsorption process, samples with various concentrations (25-200 mg/l) and a fixed pH and adsorbent dose were prepared and mixed for 100 minutes. Then, the concentration of phenol residue was measured. In order to study the effect of adsorbent dose, samples with fixed concentrations of phenol (100 mg/l) were prepared and various amounts of adsorbent (0.25-3 g) were added to them. The samples were shaken and the concentration of the phenol residue was measured according to the previous stages. In this study, the adsorption capacity was determined using the following equation:^[22]

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

where, q_e is the adsorption capacity (mg / g), C_0 is the initial concentration of phenol in the solution (mg/l), C_e is the final equilibrium concentration of phenol (mg/l), V is the liquid volume inside the reactor (l), and m is the adsorbent mass (g).

RESULTS

Analysis of the zeolite structure using XRF technique showed that the main part of its structure consisted of quartz with chemical formula of SiO_2 and its other components were Al_2O_3 , CaO , MgO , Fe_2O_3 , Na_2O , and K_2O . Based on the calculations done by Belsorb software and the use of BET isotherm, the amount of N_2 gas adsorbed by the specific surface of the adsorbent was determined as $15 \text{ m}^2/\text{g}$. The results of the pH_{PZC} showed a pH_{PZC} of 6.5 for the modified zeolite [Figure 1].

The results of the pH and the contact time are shown in Figure 2. Although the efficiency removal increased as the contact time and pH increased, phenol adsorption on the zeolite reached equilibrium after 100 minutes, and then remained constant. As shown in Figure 2, the removal efficiency at pH 3 was more than that of pH 7 and 12. The influence of concentration of phenol on its removal efficiency is shown in Figure 3. As shown in Figure 3, the adsorption capacity ($q_e = \text{mg} / \text{g}$) increased as the initial phenol concentration increased and the maximum adsorption was achieved at 200 mg / g concentration.

The results on the effect of adsorbent dose on phenol removal showed that the phenol removal efficiency increased from 65 % to 95 % as the adsorbent mass increased from 0.25 to 3 g [Figure 4]. Based on these results, the proper dose of adsorbent was determined as 1 g and was used in other parts of the study [Figure 4].

After determining the proper contact time, the adsorbent dose, and the adsorption pH, isotherm features of the given pollutant, adsorption on the modified zeolite surface was determined. The adsorption isotherm was studied through Freundlich and Langmuir general isotherm equations [Figure 5a and b]. In order to examine the conformity of the data to these adsorption models, the linear form of general equations 1 and 2 was used. Evaluation of the correlation coefficients of the two models' curves showed that phenol adsorption on the modified zeolite surface followed Langmuir adsorption isotherm and the constant coefficients of b and Q_M were 0.79 and $27 \text{ mg} / \text{g}$, respectively.^[22]

$$\frac{C_e}{q_e} = \frac{1}{bQ_M} + \frac{1}{Q_M} C_e \quad (\text{Equ. 1})$$

$$\log q_e = \log k + \frac{1}{n} \log c_e \quad (\text{Equ. 2})$$

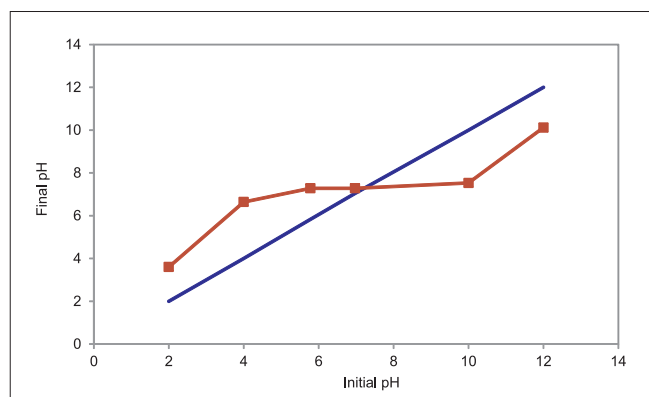


Figure 1: The pH_{PZC} curve for modified zeolite

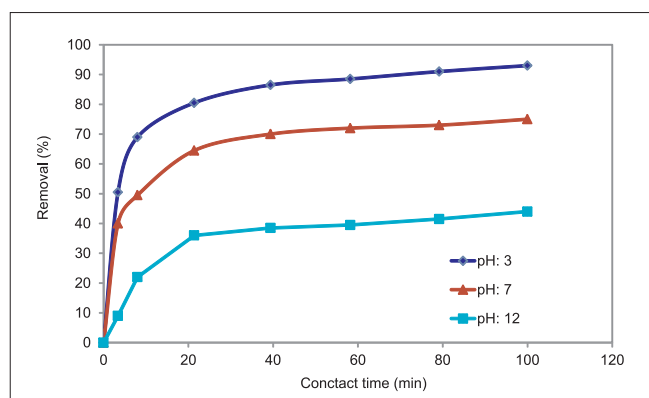


Figure 2: The effects of pH and contact time in phenol removal using modified zeolite

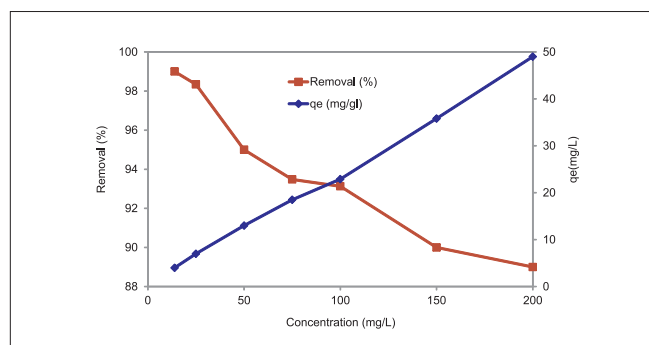


Figure 3: The effect of phenol concentration in its removal using modified zeolite

$$R_L = \frac{1}{1 + bC_0} \quad (\text{Equ. 3})$$

DISCUSSION

Determining the components of an adsorbent is one of the main points in adsorption process. The results on the components of the zeolite structure showed that the main component of the zeolite was quartz constituting 65 % of this adsorbent structure. Based on the XRF results, chemical composition of zeolite as mentioned above was determined. While zeolite is placed in water solutions, the presence

of these metal oxides causes the formation of functional groups on zeolite surface that have the most important role in adsorbing pollutants from the liquid volume. When the zeolite is modified, the functional groups on its surface will change and increase the adsorption capacity. The studies conducted by Anirudhan *et al.*, and Cpasso *et al.*, found quartz as the main component of zeolite.^[19,20]

The pH is a significant factor affecting the adsorption process through influencing phenol structure and the adsorbent surface charge. As shown by the results, phenol removal efficiency increased by increasing pH as the phenol adsorbed effectively on modified zeolite surface in pH range of 3-7. The reason is associated to the anionic structure of phenol and pH_{PZC} of the modified zeolite. The investigations show that at pH higher than pH_{PZC} , the dominant electric charge on the adsorbents surface is negative. Thus, regarding the negative surface charge of phenol at pH higher than 6.5 (pH_{PZC}), the number of negative electric charge increases by increasing pH, and considering the anionic nature of phenol, the electrostatic force of attraction between adsorbent and pollutant decreases and consequently, phenol removal efficiency is reduced.^[22,24] These results conform to the results of other studies. Banat *et al.*, reported that the percentage of phenol adsorption using bentonite was reduced while pH increased. Varghese *et al.*, also found the same results.^[11,24] These researchers have found the effect of pH on pollutant adsorption on adsorbent surface to be associated with the relationship between pH and the adsorbent surface electric

charge. They showed that at pH lower than pH_{PZC} , the adsorbent surface was surrounded by carboxylic agents containing proton that which increased the positive charge on the adsorbent surface. Considering the anionic nature of phenol ($pK_a = 10$), the electrostatic force of attraction between adsorbent and pollutant increases in such conditions and consequently, phenol removal efficiency increases, too. This phenomenon was also true for the adsorbent used in this study. Although the conditions under which this study was done differed from those of other studies, the effect of pH on phenol removal was found the same by all.

The adsorption capacity increased as the contact time increased and it reached the maximum over 100 min [Figure 2] and remained constant after this period. These results are different from the results of some other studies. A study by Qadeer *et al.*, on phenol removal by activated carbon showed that the phenol adsorption on the given adsorbent surface reached the equilibrium in less than 15 min and this result differed from the results of the present study which showed the adsorption equilibrium within 100 min.^[25] The reason of the difference may be due to the structural differences among the used adsorbents. Therefore, it can be argued that the longer time of equilibrium in phenol adsorption on the zeolite surface may be because unlike the adsorption on activated carbon taking place on its surface, the adsorption on the modified zeolite is taken place through its pores, which make the adsorption process slower than the surface areas.^[21,24,25]

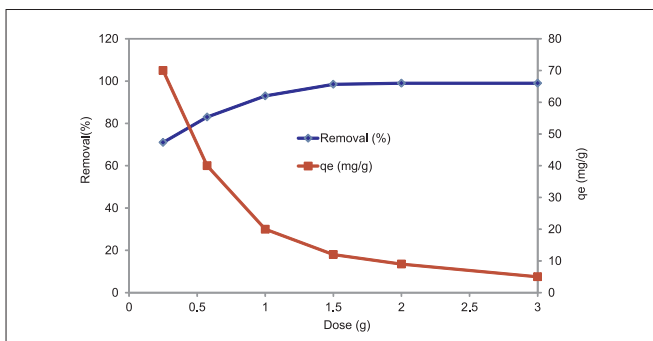


Figure 4: The effect of modified zeolite dose in phenol removal

Figure 3 shows the effect of phenol initial concentration on its removal. As shown, increasing the phenol initial concentration resulted in the reduction of removal efficiency and an increase in the phenol residue concentration. The reason is that there are specific points for adsorbing the pollutant on the zeolite-adsorbing surface which are reduced in proportion to the pollutant moles when the phenol concentration decreases. Similar results showed that phenol adsorption on the modified zeolite was reduced by increasing phenol concentration and the reason of the adsorption reduction was found the reduction of surface areas in proportion to the pollutant moles.^[26]

The optimum adsorbent dose should be determined in

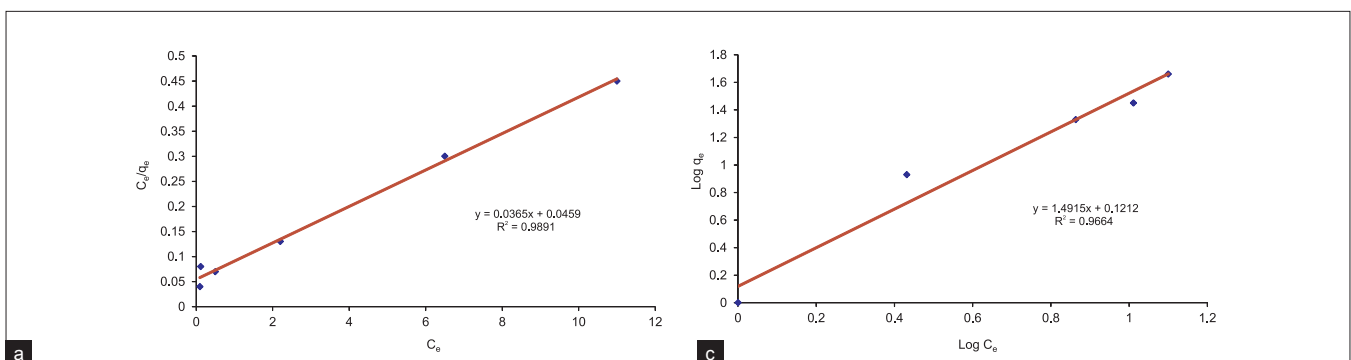


Figure 5: Isotherms of phenol adsorption on the modified zeolite surface: a) Langmuir isotherm; b) Freundlich isotherm

adsorption-related studies especially in designing large-scale systems due to the economical issues. As shown in Figure 4, phenol removal efficiency increased from 65 to 95 % as the adsorbent dose increased and it reached equilibrium at the adsorbent dose of 1 g. The increase of the phenol removal efficiency was the result of an increase in surface area which was actively effective in adsorption process.^[22,26] The results showed that despite the reduction of phenol residue by increasing the adsorbent dose, the amount of absorbed phenol decreased per unit mass of the adsorbent as the adsorbent dose increased. Although the increase of the adsorbent dose is expected to increase the active surface areas of the adsorbent and the adsorption efficiency, the results of numerous studies show the reverse. The reason is the existing unsaturated active areas on the adsorbent surface which leads to the reduction of adsorption per unit mass of the adsorbent. Qadeer *et al.*,^[25] presented similar results. Moreover, higher doses of the adsorbent per unit volume of water resulted in the adsorbent surface overlapping and aggregation of the adsorbent molecules and consequently the total surface and the pollutant adsorption decreased. The reason is that the aggregation of the adsorbent molecules increases the diffusion path during the pollutant diffusion on the adsorbent surface and this in turn decreases the adsorption efficiency.^[24,25]

The adsorption isotherm, adsorbent capacity, and the adsorption potential of the adsorbent are among the most important specifications of the adsorbent, which must be determined in adsorption-related studies. The isotherm of phenol adsorption by modified zeolite was determined using linear forms of Freundlich and Langmuir general isotherm equations [Figure 5a and b]. One of the significant parameters in adsorption equations which must be determined in order to predict the appropriateness of the adsorption is dimensionless coefficient (R_L) indicating the status of pollutant adsorption on the adsorbent surface. The $R_L > 1$, $R_L = 1$, $R_L = 0$, and $0 < R_L < 1$ show the inappropriate, linear, irreversible, and appropriate adsorption, respectively. In this study, based on the phenol initial concentration and the b-value in Langmuir isotherm equation, the value of R_L was measured as 0.0125 showing the appropriate adsorption of phenol using modified zeolite. The results of this study differ from those of some other studies.^[24,26] This difference may be referred to the surface properties of the given adsorbents.

CONCLUSIONS

The results showed that zeolite modified with FeCl₃ could be used effectively in removing of phenol. It was shown that pH was effective in phenol adsorption using modified zeolite. The removal efficiency of phenol in lower pH is more than that of in higher pH, as the efficiency changed from 93 to 35 % in pH increasing from 3 to 12. Moreover, the results showed that the removal efficiency of the modified zeolite was reduced when the contact time and dose increased. Therefore, it can be concluded that the zeolite is

a cost-effective and accessible material with an appropriate potential in phenol adsorption in comparison with the other adsorbents. Supplementary studies are required to expand the use of zeolite as an adsorbent; as the use of an adsorbent is subject to confirming the effect of all factors including the temperature, and the interaction between anions and cations.

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