

Removal of 4-nitro-phenol from wastewater using synthetic zeolite and kaolin clay

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Abstract—Adsorption techniques are widely used to remove certain classes of pollutants from wastewater. Phenolic compounds represent one of the problematic groups. Na-Y zeolite has been synthesized from locally available Iraqi kaolin clay. Characterization of the prepared zeolite was made by XRD and surface area measurement using N₂ adsorption. Both synthetic Na-Y zeolite and kaolin clay have been tested for adsorption of 4-Nitro-phenol in batch mode experiments. Maximum removal efficiencies of 90% and 80% were obtained using the prepared zeolite and kaolin clay, respectively. Kinetics and equilibrium adsorption isotherms were investigated. Investigations showed that both Langmuir and Freundlich isotherms fit the experimental data quite well. On the other hand, the adsorption of phenol was found to obey first-order kinetics.

Key words: Pollutants, Phenolic Compounds, Adsorption, Zeolite Na-Y

INTRODUCTION

Phenols are generally considered to be one of the important organic pollutants discharged into the environment. The major sources of phenol pollution in the aquatic environment are wastewaters from paint, pesticide, coal conversion, and polymeric resin, petroleum and petroleum chemicals industries. Phenol is a toxic and mutagenic substance at high concentrations and may be adsorbed through the skin. Phenols are, for the most part, biodegradable [1].

Adsorption process is efficient for the removal of organic matter from waste effluents. Natural and synthetic zeolites have gained a significant interest among scientists, mainly to their valuable properties such as ion-exchange capability. Clay minerals are also important inorganic component in soil, their adsorption capabilities come from their high-surface-area and exchange capacities. The negative charge on the clay minerals gives clay the capability to attract phenolic compounds [2].

ADSORBENT MATERIALS

1. Zeolite

Zeolites are highly porous aluminosilicates with different cavity structure. Their structures consist of a three-dimensional framework, having a negatively charged lattice. The negative charge is balanced by cations which are exchangeable with certain cations in solutions. Zeolites are usually synthesized from low cost silica-alumina sources in alkaline phase under hydrothermal conditions. The low cost silica-alumina sources are fly ash and kaolinite [3].

The characteristics and application of zeolites have been reviewed by several scientists, such as Ghobarkar et al. [4], Sircar and Myers [5] and, Breck [6]. High ion-exchange capacity and relatively high

specific surface area make zeolite an attractive adsorbent. Another advantage of zeolite over resins is their ion selectivity generated by their rigid porosity. They have been intensively studied recently because of their applicability in removing trace quantities of pollutants such as heavy metals ions and phenols. Also, they have attracted a great interest due to their catalytic and exchange properties. Molecular sieve zeolites such as 13X zeolite (also known as NaX) have been used for hydrocarbon adsorption, and later on, molecular sieves of 5A type (CaA) were also proposed [7]. Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, red mud, sludge and oxides are classified as low-cost adsorbents. To adsorb phenol selectively from water, the adsorbent must be hydrophobic. Zeolite Y owning a high Si/Al ratio, the adsorption capacity was slightly higher at low phenol concentration (<1.6 g/L) than the one of activated carbon [8].

Su et al. [9] investigated the influence of structural and surface properties of zeolite Y-templated porous carbons on phenol adsorption characteristics in the aqueous solution. They concluded that phenol adsorption in dilute solution on template-synthesized porous carbons depends on both surface oxygen groups and pore structures.

Faujasite, a natural zeolite, has similar framework composition to the Y-synthetic zeolite but is rare in nature. Where both natural and synthetic forms of the same zeolite are available in commercial quantity, the variable phase purity of the natural zeolite and the chemical impurities, which are costly to remove, can make the synthetic zeolite more attractive for specific application. Conversely, where uniformity and purity are not important, the cheapness of a natural zeolite may favor its use. Hence, natural and synthetic zeolites seldom compete for the same applications [10].

Applications in separation and purification processes often use the ability of zeolite and other molecular sieves to exclude molecules too large to enter the pores and admit smaller ones. Similarly, shape-selective catalysis takes advantage of the ability of the pores to favor the admission of smaller reactant molecules, the release of

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smaller reaction product molecules, or restriction of the size of transition-state complexes inside the micro-pores of the zeolite [11].

2. Kaolin Clay

Clay materials are strong candidates as adsorbent [12,13]. They possess a layered structure and are considered as host materials. Shichi and Takagi 2000 [14] mentioned that they (the clays) are classified by the differences in their layered structures. There are several classes of clays such as smectites (montmorillonite, saponite), mica (illite), kaolinite, serpenite, pyrophyllite (talc), and others.

The surface charge (1) has its origin in cation substitution in the structure, and hence, is pH independent; and (2) is produced by protonation/deprotonation reactions of oxide-like sites, and hence, depends on the acid and base strengths of the surface sites, as well as the ionic strength (15-17).

The adsorption capabilities result from a net charge on the structure of minerals. This negative charge gives clay the capability to adsorb positively charged species. Their adsorption properties also come from their high surface area and high porosity. Kaolin is the rock mass which is composed essentially of a clay material that is low in iron [18]. Haden and Dzierzanowski, 1961 [19] described this clay as an inexpensive, naturally occurring abundant material that was employed as a source of silica and alumina. It contains at least one of the following constituents as the chief mineral: Kalonite; Hal-lousite; Anauxite Dickite; and Nacrite. Kaolin clay is largely available in Iraq particularly in Al-Ga'ara area of western Iraq.

MATHEMATICAL MODELS

1. Adsorption Kinetics

For a solid liquid adsorption process, the solute transfer is usually characterized by either external mass transfer (boundary layer diffusion) or intraparticle diffusion or both.

Various kinetics models have been suggested for adsorption including the Lagergren pseudo-first-order kinetic, the pseudo-second order kinetics, external diffusion model, and intra particle diffusion model, which are expressed in Eqs. (1)-(4) as shown below [2,20]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

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

$$\frac{dC_t}{dt} = -k_s S(C_t - C_s) \quad (3)$$

$$q_t = -k_i (t^{0.5}) \quad (4)$$

where k_1 , k_2 , k_s , k_i are the pseudo-first order, pseudo-second order rate constants, mass transfer coefficient, and rate parameter of the intraparticle diffusion control stage, respectively, q_e the amount of solute adsorbed (mg/g) at equilibrium and q_t the amount of solute on the surface of the adsorbent (mg/g) at any time t , C_s and C_t are surface and solution concentration, and S is the specific surface area. Most of the investigations on the adsorption kinetic of phenolic compounds onto low-cost adsorbents stated that it usually follows the first-order kinetics and that the adsorption is pore diffusion controlled.

2. Adsorption Isotherms

The Langmuir and Freundlich isotherms are both used to describe observed adsorption phenomena of phenolic compounds onto dif-

ferent adsorbents. The Langmuir isotherm applies to adsorption on completely homogeneous surface with negligible interaction between adsorbed molecules. For a single solute, it is given by [21]:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (5)$$

The linear form can be written as:

$$\frac{1}{q_e} = \frac{1}{q_m} + \frac{1}{q_m b C_e} \quad (6)$$

where C_e is the equilibrium concentration of the solution, q_e is the amount adsorbed per unit mass of adsorbent, m is the mass of the adsorbent, q_m is the monolayer capacity, and b is an equilibrium constant that is related to the heat of adsorption by equation.

The Langmuir model can describe most adsorption phenomena of phenols on different adsorbents. In most cases, q_m and b increase with temperature, suggesting that adsorption capacity and intensity of adsorption are enhanced at higher temperature. The Freundlich model, which is an empirical model used to describe the adsorption in aqueous systems, was also used to explain the observed phenomena of adsorption. The Freundlich isotherm is shown as the following equation [22]:

$$q_e = K_f C_e^{1/n} \quad (7)$$

The linear form of the equation can be written as:

$$\log q_e = \log K_f + \log C_e^{1/n} \quad (8)$$

where K_f is the measure of adsorption capacity, $1/n$ is adsorption intensity. A plot of $\log(q_e)$ against $\log C_e$ gives a straight line, the slope and intercept of which correspond to $1/n$ and $\log K_f$, respectively.

The Redlich-Peterson model is also used to describe the observed adsorption phenomena of phenolic compounds. This isotherm/equation has three parameters, A , B , β . Parameter β ranges between 0 and 1. The equation is represented below [1]:

$$\frac{C_e}{q_e} = \frac{B}{A} + \frac{1}{A} C_e^\beta \quad (9)$$

This isotherm describes adsorption on heterogeneous surfaces, as it contains the heterogeneity factor β . It can be reduced to the Langmuir equation as β approaches 1; the parameters A , B , β are determined by curve fitting.

The Temkin isotherm model contains a factor that explicitly takes into the account adsorbent-adsorbate interactions [23]. The linearized form of this model is as follows:

$$(q_e = RT/(bT) \ln A_T + (RT)/(bT) \ln C_e) \quad (10)$$

EXPERIMENTAL WORK

1. Zeolite Na-Y Synthesis

Na-Y zeolite was prepared from locally available kaolin; other materials used in the preparation, which are sodium hydroxide (97% purity) and sodium silicate (99% purity), were of analytical grade. The procedure used for zeolite preparation is summarized as follows [24,25]:

Kaolin (<75 μm), mixed with 45% NaOH as weight ratio (kaolin/pure NaOH)=(1/1.5), was fused at 850 $^\circ\text{C}$ for 3 hours. Sixty grams of the fused kaolin was mixed with 72 grams of sodium silicate and

dispersed in 900 ml of deionized water in a batch reactor. Agitation speed and flask temperature were kept constant using a regulator attached with an electrical magnetic stirrer. The gel formation step was achieved at 60 °C and atmospheric pressure during one hour. The resultant slurry, which has pH of 13.6, was placed in a 1,000 ml sealed glass jar, and subjected to ageing at 50 °C for 24 hr in a programmable electrical furnace; then the gel slurry was subjected to hydrothermal crystallization at 100 °C for 48 hr. After filtration, washing with deionized water to pH of 11.5, the crystalline mass was dried at 100 °C for 16 hr and activated at 500 °C for 1hr. The prepared zeolite was characterized by XRD test (Shimadzu, Japan XRD-6000). Langmuir and BET surface area and pore volume were made by N₂ adsorption at 77 K and p/p^o (0-0.3).

2. Adsorption Study

Different concentrations of Nitro-Phenol aqueous solutions were prepared from a stock of 500 mg/l solution prepared from analytical grade.

The equilibrium isotherms were determined by mixing 0.5 g of zeolite (or kaolin) with of 25 ml of nitro-phenol solution in conical flasks of different concentrations (20, 40, 80 and 100 mg/l). Flasks were shaken at 200 rpm overnight to assure that equilibrium was reached. The residual concentration was analyzed using UV visible spectrophotometer (UV-1600 Shimadzu, Japan) at wave length 320 μm. The adsorbed amount was calculated by the following equation:

$$q_e = \frac{(C_o - C_e)V}{W} \quad (11)$$

where q_e is the amount adsorbed at equilibrium, v volume of solu-

tion, C_o is the initial concentration, C_e is the concentration at equilibrium and w is the amount of adsorbent.

The adsorption kinetics were investigated by adding 0.5 gram zeolite (or kaolin) to 25 ml of 40 mg/l of nitro-phenol solution. Samples were analyzed at different time intervals. The effect of adsorbent dosage and the initial concentration of the feed solution were also studied using different amount of the adsorbent (0.5, 1, and 2 grams) for the former and different initial concentrations (20, 40, 80, 100 gm/l) for the latter. All the samples were shaken at constant speed of 200 rpm and analyzed by the same spectrophotometer aforementioned.

RESULTS AND DISCUSSION

1. Characterization

The prepared zeolite from Iraqi kaolin clay was characterized using XRD technique. It can be seen from Fig. 1 that good crystallinity of zeolite Y with traces of zeolite P and that zeolite Y appeared in the proper maximum peak of $2\theta(6.181)$, which was stated earlier that it must be within (6-10) [26]. Si/Al ratio was found as 1.34 : 1. Typical values for zeolite Y, which display Si : Al ratio, are in the range of 1.5 : 1-3 : 1 [27]. Langmuir and BET surface area and pore volume are given in Table 1. The isotherm plot as represented by

Table 1. Surface area and pore volume for the prepared zeolite

| Langmuir surface area | BET area | Pore volume |
|---------------------------|---------------------------|--------------------------|
| 227.812 m ² /g | 156.876 m ² /g | 0.150 cm ³ /g |

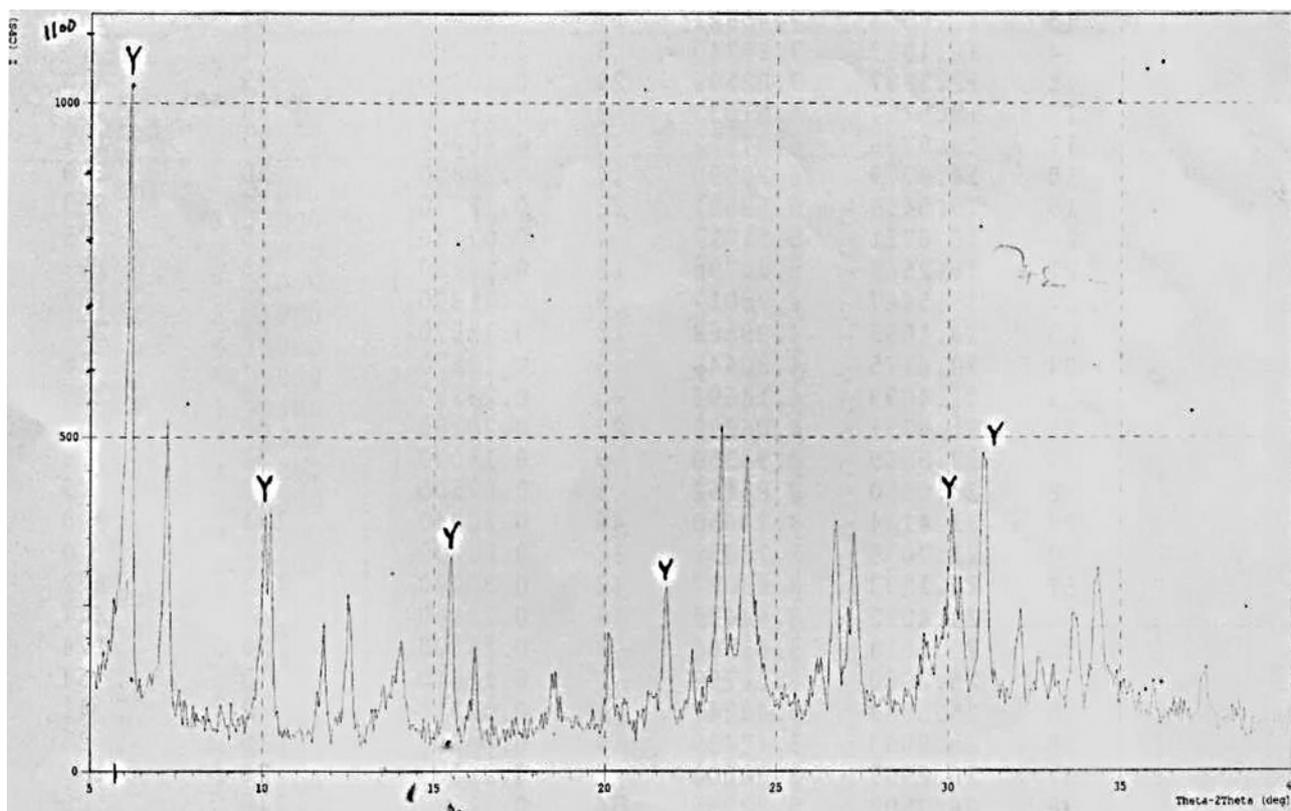


Fig. 1. XRD pattern for the prepared zeolite.

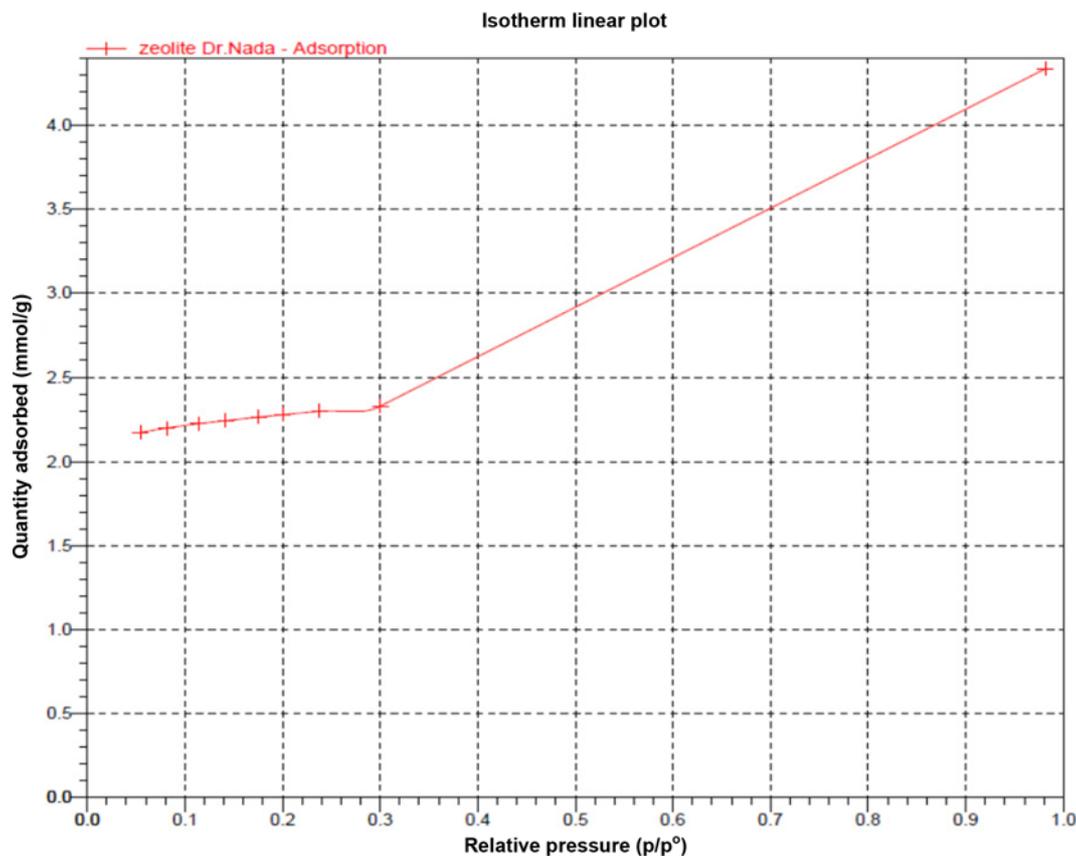


Fig. 2. The quantity adsorbed(mmol/g) of N₂ at 77 K vs. relative pressure (p/p^o).

the amount adsorbed vs. relative pressure is shown in Fig. 2.

2. Equilibrium Isotherm

Experimental data of phenol adsorption on prepared zeolite Y was manipulated to fit different isotherm models. Langmuir, Freundlich, Temkin and Redlich-Peterson models were investigated and their parameters are listed in Table 2. Both Langmuir and Freundlich isotherms were found to give the best fit. However, the other

Table 2. Equilibrium parameters for isotherm models

| Model | Parameter | Kaolin | Zeolite | |
|------------------|---|--------|---------|---------|
| Langmuir | q_m (mg/g) | 7.7459 | 10.8340 | |
| | $q_e = \frac{q_m b C_e}{1 + b C_e}$ | b | 0.00999 | 0.0183 |
| | R^2 | 0.9988 | 0.9984 | |
| Freundlich | K_f | 0.107 | 0.2298 | |
| | $q_e = K_f C_e^{1/n}$ | 1/n | 0.819 | 0.849 |
| | R^2 | 0.9919 | 0.9999 | |
| Temkin | $q_e = (RT/b) \ln(AC_e)$ | A | 0.343 | 0.1916 |
| | $B = (RT/b)$ | B | 1.5789 | 1.0892 |
| | R^2 | 0.9796 | 0.9618 | |
| Redlich-Peterson | A | 3.8240 | 3.0450 | |
| | $\frac{C_e}{q_e} = \frac{B}{A} + \frac{1}{A} C_e^\beta$ | B | 46.7112 | 14.2693 |
| | β | 0.85 | 0.62 | |
| | R^2 | 0.9085 | 0.9805 | |

two models may also be considered as having good representation. Langmuir assumes a homogeneous mono layer adsorption, while the Freundlich assumption is based on the heterogeneity of the surface of the adsorbent. The value of the exponent in Freundlich models assures surface heterogeneity along with correlation coefficients [28]. The value of the exponent (1/n) as it is closer to one indicates low affinity to the adsorbate at low concentration [29]. Separation factor (r) as defined by Eq. (12) was calculated and found to be (0.5 and 0.35) for kaolin and zeolite, respectively, which reflects the favorable adsorption of 4-nitrophenol on both adsorbents. A review of some previous isotherms is given in Table 3.

$$r = \frac{1}{1 + bC_0} \tag{12}$$

3. Kinetics

Adsorption of 4-nitrophenol on prepared zeolite and kaolin clay was tested for different kinetic models. Initial concentration of the adsorbate was 40 mg/l and 0.5 g of each adsorbent was used. The adsorption process obeys the pseudo first-order Lagergren equation. Adsorption constants with the correlation coefficients are given in Table 4.

4. Effect of Adsorbent Loading

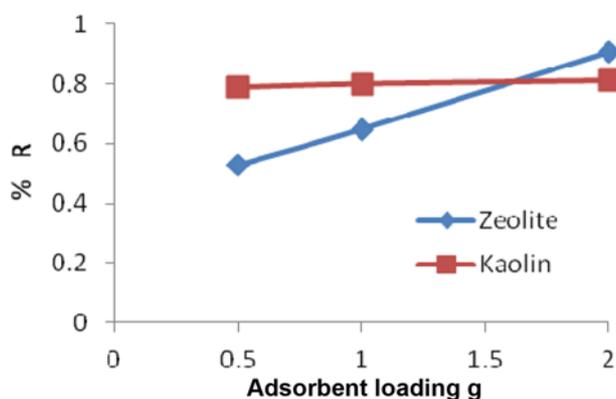
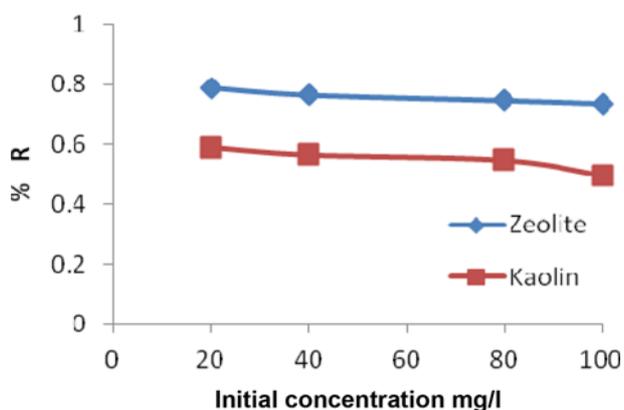
This effect was studied using three different amounts of each adsorbent (zeolite and kaolin). 0.5, 1, and 2 g were tried using the conditions of constant initial concentration of 40 mg/l of 4-nitrophenol. Fig. 3 shows that by increasing zeolite loading the removal of the pollutant was also increased, reaching the highest value of 90.6%

Table 3. Review of some previous isotherm models

| Adsorbent | Langmuir | | Freundlich | | Reference |
|----------------------------|--------------|------------|------------|-------|------------------------------|
| | q_m (mg/g) | b (l/mg) | K_f | n | |
| Phanerochaete biomass | ----- | ----- | 0.187 | 1.21 | Wu J and Yu HQ (2006) [30] |
| Coal fly ash | 2.730 | 0.00917 | 1.88 | 1.77 | Batabyal et al. (1995) [31] |
| South african coal fly ash | 0.11 | 0.042 | 0.115 | 1.267 | Potgieter et al. (2009) [29] |

Table 4. Kinetics parameters

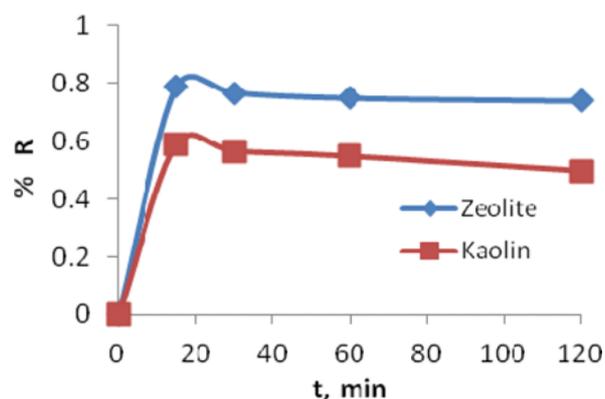
| | Pseudo-first-order | Pseudo-second-order | Intra-particle diffusion |
|---------|---|---|---|
| Zeolite | $k_1=0.0308$ (min^{-1}) $R^2=0.962$ | $k_2=0.0359$ ($\text{mg}/(\text{mg}\cdot\text{min})$) $R^2=0.116$ | $k_i=0.3329$ ($(\text{mg}/\text{g})/\text{min}^{0.5}$) $R^2=0.945$ |
| Kaolin | $k_1=0.0302$ (min^{-1}) $R^2=0.947$ | $k_2=-0.0083$ ($\text{mg}/(\text{mg}\cdot\text{min})$) $R^2=0.425$ | $k_i=0.2338$ ($(\text{mg}/\text{g})/\text{min}^{0.5}$) $R^2=0.938$ |

**Fig. 3. Effect of adsorbent loading on the percent removal of 4-nitrophenol.****Fig. 4. Effect of initial concentration of 4-nitrophenol on the percent removal.**

using 2 g. While kaolin clay behavior was different, for the removal seems to reach constant value of 80%. This can be attributed to the higher surface area of zeolite in comparison to kaolin clay which normally falls within the twenties.

5. Effect of Initial Adsorbate Concentration

The initial concentrations of 4-nitrophenol ranging between 20-100 mg/l were investigated. Results are drawn in Fig. 4. Percent

**Fig. 5. The effect of time on the removal of 4-nitrophenol on the prepared zeolite and kaolin clay using 40 mg/l and 0.5 g of the adsorbent.**

removal was found to decrease as the initial concentration increased on both adsorbents. The reason for this behavior can be clarified by that the adsorption sites will be filled with the adsorbate until there is a time where the increasing amount of the adsorbate does not have available sites to get in. Besides, the concentration gradient between the bulk and the surface will be decreasing so that some of the adsorbate will not have a host site.

6. Effect of Time

Increasing the time of mixing increased the removal efficiency. Adsorption was found to increase in the first fifteen minutes so that about 78% of the pollutant was removed using zeolite and about 60% on kaolin clay. As time elapsed, a constant removal was obtained; however, some fluctuations happened during the two hours. Fig. 5 shows the effect of time on the percent removal.

CONCLUSIONS

Adsorption of 4-nitro phenol in dilute solutions on synthesized zeolite Na-Y and Iraqi kaolin clay was investigated. It was found that the removal increased by increasing adsorbent loading and time of mixing and with the decrease of the initial concentration. This conclusion was true for both adsorbents, but zeolite performance was better due to the higher surface area and better ability of zeolites to

adsorb guest molecule inside their porous structure. Equilibrium isotherms suggested a favorable adsorption of mono layer with some heterogeneity of the surface as they follow Langmuir and Freundlich models very well. Finally, the rate of the adsorption was described by pseudo first-order equation.

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