Adsorption of Phenol from Aqueous Solutions by Local Egyptian Bentonite

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Abstract: Phenolic compounds are some of the major hazardous compounds in industrial wastewater due to their poor biodegradability, high toxicity and ecological aspects. These compounds are listed by US Environmental Protection Agency (EPA) among the priority pollutants for instance phenols are released into water from industrial effluent discharges such as petroleum refinery wastewater. Classical methods employed for phenol removal are either costly or limited to large-scale applications such as biological and thermal decomposition methods. In this study an Egyptian Bentonite clay has been used for the adsorption of phenol from aqueous solutions over a concentration range of 10–100 mg/l, shaking time of 5–120 min, stirring rate from 50-250 r.p.m and adsorbent dosage from 0.1to 0.5 g. The Experiments were carried out for the analysis of adsorption equilibrium capacities using a batch equilibrium technique. The process of uptake follows both the Langmuir and Freundlich isotherm models. The complete removal of phenol was observed with initial concentration of 10 mg/l and 0.5 g of bentonite, speed rate of 200 r.p.m. with 30 min time of contact. All Experiments were done at room temperature.

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1. Introduction

Petroleum products have vast uses in modern society. Phenols are important industrial chemicals of environmental concern since they are widely used in many industries such as coke, refineries, manufacturers of resin, pharmaceuticals, pesticides, dyes, plastics, explosives and herbicides, and can also occur in their wastewaters. Phenols are produced in very large quantities for use as solvents, and starting materials for chemical synthesis [1]. Phenols are released into water from industrial effluent discharges such as petroleum refinery wastewater. It has also been detected in groundwater as a result of leaching through soil after a spill of phenol from landfill sites. Typical wastewaters from oil refineries contain phenol in concentrations ranging from 5,000 to 15,000 mg/L, and those from coking plants in concentrations ranging from 200 to 6,000 mg/L [2]. The presence of phenol in drinking water and irrigation water represents a serious health hazard to humans, animals, plants and microorganisms [3]. Due to the high toxicity of phenols, they are subjected to specific regulations. The Environmental Protection Agency (EPA) calls for lowering phenol content in potable and mineral waters to 0.5 ppb, while the limits for wastewater emissions are 0.5 ppm for surface waters and 1 ppm for the sewerage system [4].

There are different methods for the separation of phenols such as steam distillation [5], Separation by extraction [6], Separation by membrane [7, 8], Destruction of phenol by air oxidation [9-13], Electrochemical oxidation [14-16], Biochemical abatement [17]. Many problems associated with the above mentioned methods have been reported in the

literature such as high cost, low efficiency and generation of toxic products [18]. However removal of organic compounds by adsorption on bentonite has a little work in literature survey [19-20]. Most of works on adsorption of organic compounds from industrial waste have been done by using the traditional activated carbon as an adsorbent. Among viable options of adsorbent material of low cost is the local Egyptian bentonite. Bentonite is an adsorbent aluminum phyllosilicate and is mainly composed of montmorillonite (smectite) with some other clays and inorganic minerals [21-22]. Types of bentonites depend on their dominant elements (K, Na, Ca and Al). Such clay minerals in soil play the role of natural scavenger by removing and accumulating contaminants in water passing through the soil through exchange adsorption mechanism. The high specific area and the ability of holding water in the interlayer sites gave clays excellent adsorbent capacity which could be increased by acid activation and/or thermal treatment [23]. In the present study, effective removal of phenol from simulated waste water has been studied by using natural Egyptian bentonite with Al/Si ratio 1:3.4 by weight as an adsorbent after optimization of the adsorption conditions.

2. Material and Methods

2.1. Reagents and analytical procedures

A stock solution of phenol was used in adsorption experiments prepared by using an analytical grade chemical and dissolving it in distilled water. Experimental solutions of the desired concentrations were obtained by successive dilution with distilled water. The pH of the solution was adjusted by means of HCl and/or NaOH solution using digitally calibrated pH-meter ((HaNNa, Model pH 211) .The analytical determination of phenol was carried out with the standard spectro photometric procedure ^[24] using U.V spectrophotometer (UNICO, Model U.V 2100). At the end of each experiment, the treated solutions were filtered by using Whitman No. 40 filter paper, before analysis.

2.1.1. Characterization of Adsorbent

The clay used in this work was obtained from Sphinx milling station Company (Alexandria free zone). Activated bentonite is brown in color; it was characterized by x-ray florescence (XRF) using AXIOS PANalytical2005, The analysis was made in Central Metallurgical Research Institute in Alexandria. Table (2.1) shows the oxides constituents of the studied bentonite clay. A scan electron microscope with different magnification was done on dry base for a sample of clay to specify the morphological features of natural bentonite. This was done in laboratory of faculty of science in Alexandria University as shown in Figs. (1, 2). Natural bentonite has low alumina content (16.14%) and contains high silica contents (55.12%). Bentonites show higher distribution of alkali oxides. There is general agreement between the current obtained values for both major oxide contents and the high loss on ignition percentage (12-15%) with the calculated values and recorded results previously obtained for Egyptian kaolin and bentonite [25-27]. The Variables Investigated in this study are the Effect of amount of adsorbent, initial phenol concentration, and time of mixing.

Oxides	Wt.%	
SiO ₂	55.12	
Al ₂ O ₃	16.14	
Fe ₂ O ₃	8.25	
CaO	1.17	
TiO ₂	1.18	
MgO	2.86	
K ₂ O	1.05	
Na ₂ O	1.41	
L.O.I	12.35	

TABLE 2.1. Chemical Characterization of bentonite



FIGURE 2. Scanning electron microscope (SEM) of dry bentonite with another magnification.

3. Results and Discussion

3.1. Effect of Time

Figures (3.1) and (3.2) indicate the effect of contact time for phenol at different concentrations on

residual concentration and percentage removal respectively. It was found that as the contact time between adsorbent and adsorbate increases the percentage removal increases and the residual concentration of phenol decreases. In the first 15 mins, the rate of adsorption was apparently fast, which can be explained that the available adsorption sites were sufficient compared with the density with the bare surface of the adsorbent in the beginning. As the process goes on, the adsorption sites became saturated gradually. The uptake rate was controlled by the rate at which the adsorbate transported from the exterior to the interior sites of the adsorbent particles, so the adsorption became much slower [28].



Figure 3.1. Effect of Time on the Residual Concentration of Phenol (Temp = 25° C, Speed of shaking = 200 rpm, Amount of bentonite = 0.5 gm ,Volume treated =100 ml).



Figure 3.2. Effect of Time on the Percentage Removal of Phenol ($Temp = 25^{\circ}C$, Speed of shaking = 200 rpm, Amount of bentonite = 0.5 gm,and Volume treated=100ml).

3.2. Effect of adsorbent dosage

The influence of bentonite mass on percentage removal and residual concentration of phenol were shown in figures (3.3) and (3.4) .These figures have showed that as the amount of bentonite increases from 0.1 g to 0.5 g. The percent removal of phenol increases from 35.5 % to 75.5 % and residual concentration

decreases from 38 mg/L to 11mg/L. From those results it was found that the optimum dosage of bentonite for phenol was 0.5 g. [Crown and White (29) have observed similar results for phenol]. This may be due to those higher amounts of bentonite means availability of a larger surface area or a larger number for adsorption sites [30] and therefore, higher capacity for adsorption.



Figure 3.3. Effect of the Amount of Bentonite on the Residual Concentration of Phenol ($C_0 = 40$, Temp = 25^oC, Speed of shaking = 200 rpm, Volume treated = 100 ml).



Figure 3.4. ($C_0 = 40$, Temp = 25^oC, Speed of shaking = 200 rpm, Volume treated = 100 ml).

3.3. Effect of shaking speed (r.p.m)

Figure (3-5) shows the effect of shaking speed (r.p.m) on the percentage removal of phenol. It was observed that as the speed of mixing rotation increases from 50 to 250 r.p.m the percentage removal increases

from 10 % to 86.25%. And this was attributed to the fact that as the rotation speed increases there was a good mixing between the adsorbate and the adsorbent from figure. The optimum speed for all experiments is taken to be 200 r.p.m.



Figure 3.5. Effect of Speed on the Percentage Removal of Phenol ($C_o = 40 \text{ mg/L}$, Temp = 25^oC, Amount of bentonite = 0.5gm, Volume treated =100 ml).

3.4. Effect of the Initial Phenol Concentration

Figure (3.6) indicates the effect of initial concentration of phenol on the residual concentration of the solution. It was found that as the initial concentration of phenol increases from 10 mg/L to 50 mg /L the residual concentration increase from4mg/L to15mg/L. From figure it is evident that at high concentration, the available sites of adsorption become fewer. This behavior is connected with the competitive

diffusion process of the phenol through the microchannel and pores in bentonite. This adsorption of phenol will lock the inlet of channel on the surface and prevent the ions from passing deeply inside the bentointe. The adsorption occurs on the surface only. Similar results in recent studies using natural zeolite [31] and olive cake [32], in addition to what have been found by karthikeyan et al. [33].



Figure 3. 6. Effect of the Initial Concentration on the Residual Concentration of Phenol Amount of bentonite = 0.5gm, Temp= 25° C, Speed of shaking = 200 rpm, Volume treated = 100 ml).

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3.5. Adsorption isotherm

Adsorption isotherms of bentonites for phenol was expressed mathematically in terms of the Langmuir and Freundlich models. The obtained experimental data are commonly well fitted with the Langmuir (Eq. (3.1)) and Freundlich (Eq. (3.2)) models. The linearization of these two equations gives Eq. (3.3) and Eq. (3.4).

$$q_e = \frac{K_L * C_e}{1 + aC_e} \tag{3.1}$$

$$q_e = K_F * C_e^n \tag{3.2}$$

If these equations are rearranged to the linear form: then.

$$\frac{C_{e}}{q_{e}} = \frac{1}{\kappa_{L}} + \frac{a}{\kappa_{L}} * C_{e}$$
(3.3)

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{3.4}$$

Where $K_{\rm L}$, a and $K_{\rm F}$, n are the constants for Langmuir and Freundlich models, respecti. The value of 1/n is less than 1 indicating that bentonite is a good adsorbing material for phenol. In addition to the experimental data, the linearzed forms of Langmuir and Freundlich isotherms using the above equation for phenol removal by bentonites are given Figs. (3.7) and (3.8).







Figure 3.8. Freundlich plot for the Adsorption of Phenol on Bentonite ($C_o = 40 \text{mg/L}$, Temp=25^oC, Speed of shaking = 200 r.p.m, Volume treated =100 ml).

3.8. Morphology study

In this study, SEM is used to probe the change in morphological features of natural bentonite and phenol adsorbed on bentonite (Fig. 3.10). It is clearly observed in Fig. (3.11) & Fig. (3.12) that the surface morphology of phenol adsorbed on bentonite is different from that of natural bentonite only. The natural bentonite clay shows loose aggregates with porous structure. After adsorption, large amounts of pores on clay disappear with an increase in adsorption time and as the adsorption time reaches 30 min the surface of the clay demonstrates compact aggregates and does not change visibly with further adsorption. SEM results show that the surface morphology of the bentonite clay changed evidently during the adsorption process, indicating that an important interaction at the phenol – granule interface occurred in the experimental conditions.



Figure 3.9. Scanning electron microscope (SEM) of dry "natural" bentonite before Adsorption.



FIGURE 3.10. Scanning electron microscope (SEM) of phenol adsorbed on bentonite before Adsorption.



Figure 3.11. Scanning electron microscope (SEM) of phenol adsorbed on bentonite after adsorption.

4. Conclusions

Egyptian bentonite is capable of removing phenol solution as investigated in the present study. The following **conclusions** can be drawn based on this investigation:

- 1. The adsorption characteristics of phenol are strongly affected by initial solution concentrations, amount of bentonite dosage speed of shaking and time of mixing.
- 2. It has been found that the amount of phenol adsorption on natural bentonite increases with increasing contact time (time of mixing) at all initial phenol concentrations and equilibrium is attained within 30 min for phenol so that the residual concentration of phenol will decrease and the percentage removal will increase with increasing contact time respectively.

- 3. The increase of the initial concentration of phenol leads to the increase of the residual concentration and decrease of the percentage removal.
- 4. The experimental data for phenol is well fitted to both the linearized Langmuir isotherm and the linearized Freundlich isotherm.

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