ORGANOCLAY FOR ADSORPTION OF BINARY SYSTEM OF POLLUTANTS FROM WASTEWATER

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ABSTRACT

single and binary competitive sorption of phenol and p-nitrophenol onto clay modified with quaternary ammonium (Hexadecyltrimethyl ammonium) was investigated to obtain the adsorption isotherms constants for each solutes. The modified clay was prepared from blending of local bentonite with quaternary ammonium . The organoclay was characterized by cation exchange capacity. and surface area. The results show that paranitrophenol is being adsorbed faster than phenol . The experimental data for each solute was fitted well with the Freundlich isotherm model for single solute and with the combination of Freundlich-Langmuier model for binary system .

الخلاصة

تم دراسة الامتزاز لنظام احادي والامتزاز التنافسي لنظام ثنائي للفينول و بارا- نايترو الفينول على سطح الطين المعامل بالامين الرباعي للحصول على ثوابت الامتزاز لكل ملوث . تم تحضير الطين العضوي من مزج البنتونايت المحلي مع الامين الرباعي . ومن ثم فحص الطين العضوي المحضر عن طريق قياس قابلية الطين العضوي للتبادل الايوني الموجب وكذلك فحص المساحة السطحية . بينت النتائج ان بارا- نايتروفينول يمتز اسرع من الفينول وكانت النتائج العملية مطابقه لمعادلة فريندلج بالنسبة للانظمة المنفردة ولمعادلة فريندلج لانكماير للانظمة الثنائية .

KEY WORDS

Organoclay, adsorption, Freundlich model, wastewater

INTRODUCTION

In recent years , there were a wide range of hazardous waste disposal and contaminated of water in which affect on human health and environmental .The transport of these compounds in the environment is a complex process, depending on such factors as solubility, octanol-water partition coefficient , chemical and biological reactivity . Adsorption process is widely used for removing organic compounds from water.

Phenolic compounds are toxic if adsorbed through the skin and may result in death. Contact with the skin also causes dangerous and painful burns. Immediate washing of the skin with ethanol solution and warm water usually removes the phenolic compounds without serious consequences. Phenol and its derivatives induces toxic effect for fish and aquatic life. They induce genotoxic ,carcinogenic, immunotoxic, hematological and physiological effects and have a high bioaccumulation rate along the food chain due to its lipophilicity . Thus phenol pollution represents a threat against natural environment and also to human health. When phenol is present in the aquatic environment, fish food consumption ,mean weight and fertility are significantly reduced. Excessive exposure may affect the brain, digestive system, eye, heart, kidney, liver, lung, peripheral nerve, skin and the unborn child . The Environment agency aims to ensure that environmental exposures are too low to cause such effects. [Gad and Saad,2008].

Clay is a representative of 2:1 layered phyllosilicates. These layers are built from two tetrahedral and octahedral cations can be replaced by lower valence cations, such as Al^{+3} and Fe^{+2} or Mg^{+2} respectively. The excessive negative charge of these layers is compensated by metal cations (Na^{+1}, K^{+1}, Ca^{+2} and Mg^{+2}) in the interlayer space, which can be exchanged with various cations, such as quaternary ammonium salts forming the modified clay (organoclay).[Jaynes and Boyd,1991].

Natural clay is ineffective sorbents for removal of toxic organic compounds from environment. The inorganic exchange cations of natural clays are strongly hydrate in water, producing a hydrophilic environment at the clay surface. The replacement of inorganic exchange cations with organic cations of alkyl hydrocarbon yields organoclay with organophilic properties [Boyd et al,1988].

Boyd and Jaynes, (1992) divided organoclays into two types, organophilic and adsorptive . Organophilic clays are formed using large alkyle cations, and adsorptive organoclays are formed using small alkyl or small aromatic organic cations. Smith and Galan,(1995), found that organoclays prepared using small organic cations have internal surfaces which can act as hydrocarbon adsorption sites . The objectives of this study are to modify the natural clay to organoclay and to investigate the competitive adsorption between phenol and p-nitrophenol onto prepared organoclay.

- MATERIALS AND METHOD

Adsorbates

Phenolic compounds namely as; phenol and p-nitrophenol were used as adsorbates. These physical properities are listed in table (1).

- Adsorbent (Organoclay)

The organoclay was prepared by adding the required quantity of hexadecyltrimethyl ammonium chloride solution (25% wt./vol.) to the desired quantity of bentonite in a stainless steel container. The bentonite used in this study was a local bentonite in powder form (particle size of 0.075mm) calcium type . It was supplied by the State Company of Geological Survey and Mining (Baghdad) The resulting paste was then introduced into the meat grinder to achieve good mixing . The product was dried in the electrical oven at 85 ºC for 48 hours and then ground by agate mortar and screened to desirable particle size of (0.075mm) . The physical properties of the prepared organoclay was measured at the laboratories of the Ministry of Industry and Minerals (Ibn Sina State Company) and at the Ministry of Oil (Institute of Oil Training and Development).The results are presented in Table (2).

Procedure

A series of batch experiments were carried out to determine the adsorption isotherms of Ph and pnp solutions onto organoclay with pH of 6.5-6.8. A certain amount of organoclay (0.05, 0.1, 0.15, 0.2, …….0.5 g) was placed into 100ml contaminant solution at concentration of 0.05kg/m^3 for each solute . The adsorption experiments were conducted at constant shaking at room temperature for 30 hour to achieve equilibrium concentrations. Then, the solutions were filtrated, and their concentration were determined by UV-spectrophotometer at college of engineering, Baghdad university (Model UV-GENESYE TM 10) at λ_{max} =270nm and λ_{max} =317nm for ph and pnp respectively. The adsorption capacity q_e (kg/kg) of each solute onto organoclay was calculated by mass balance relation :

$$q_e = \frac{V(C_o - C_e)}{W} \qquad (1)$$

Where C_o and C_e are the initial and equilibrium concentration of adsorbate respectively (kg/m^3), V is the volume of solution and W is the weight of the organoclay used (kg).

RESULTS AND DISCUSSION

Characterization of Modified Clay

In order to examine the structural difference of the clay before and after modification with a quaternary amine, clay and their modified organic derivatives are characterized using ordinary as well as modern characterization tools which include determination of cation exchange capacity, surface area and total organic carbon (Hasmukh et al., 2006) as described below:

Cation Exchange Capacity

The clays are characterized by their cation exchange capacities , which can vary widely and depend on source and type of clay.

Cation exchange capacity (CEC) is represented by the weight ratio of amine to bentonite. The cation exchange capacity for Iraqi bentonite is about 80 meq/100gm bentonite (according to the specifications of the supplier) . The weight ratio of amine to bentonite was calculated from its relation with cation exchange capacity percentage. The CEC was calculated according to the following equation [Mousavi et al., 2006] :

$$\frac{\text{Amount of amine, g}}{100g\ \text{bentonite}} = \frac{\text{MW. of amine, g/g.mole} \times \text{CEC, meq/100g} \times \%\text{CEC}}{1000} \qquad (2)$$

where 80 meq/100gm bentonite represents 100% CEC and molecular weight of amine is 320 g/g mole . The appropriate equation to satisfy this above equation is found to be:

g amine /100g bentonite =0.256 %CEC

or : Y=0.256 X (3)

Where : Y is g amine/100g clay and X is %CEC .The results are tabulated in Table (3) **:**

To choose the best ratio of amine to clay for maximum removal efficiency, a shaker speed of 200rpm was run for 10 hours, containing 0.5g of prepared organoclays (given in Table 2) and 100ml of water polluted with 50ppm of each solute.

The results are depicted in Table (4) indicating the large effect of amine to bentonite ratio on the removal efficiency and as can be seen an increase of the ratio increases the removal efficiency , reaching a maximum value of 35g/100g clay for each solute at 136.72 %CEC . Above this weight ratio no effect on removal efficiency is obtained ,where the effluent concentrations of Ph and pnp decrease to 8, 5.8 and mg/l respectively.

Alberto et al., (2002) characterized the organophilic clay used in the solidification/stabilization of hazardous waste at %CEC of 150 meq/100g. In this cement-based stabilization/solidification processes hae been used for about two decades for the immobilization organics pollutants in hazardous wastes and contaminated soils.

SURFACE AREA

The surface area of natural clay is found to be 65 m^2 /g . For an organoclay this decreased to 37.6 m^2/g (Institute of Oil Training and Development). Because organoclay is more aggregated than natural clay. The low value of the surface area found with the organoclay was because measurements were made at the external surface only, no internal surface area was accessible to nitrogen .This reason was stated by [Jaynes and Vance,1996]. This may be also attributed to the nearly total blocking of the micropores by the surfactant loaded material.

Estimation of Adsorption Isotherms Constants

The adsorption of a single and binary compound systems of phenol and paranitrophenol onto organoclay in batch experiments were conducted with initial concentration of (0.05 kg/m^3) and particle size of (0.075 mm)at room temperature in order to determine the isotherms constants for each system using different models as follows: (Nasir,2010)

- **Freundlich model**

$$q_e = KC_e^{1/n} \tag{4}$$

- **Langmuir model**

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{5}$$

- **Radk-Prausnitz model**

$$q_e = \frac{K_{RP} C_e}{1 + \left(\frac{K_{RP}}{F_{RP}}\right) C_e^{1-N_{RP}}} \tag{6}$$

- **Combination of Langmuir-Freundlich model**

$$q_{e,i} = \frac{q_{m,i} b_i C_{e,i}^{1/n_i}}{1 + \sum_{i=1}^{N} b_i C_{e,i}^{1/n_i}} \tag{7}$$

Single Component System

The adsorption isotherms for single component systems of phenol and p-nitrophenol onto organoclay are shown in figures 1 and 2

Binary Component System

The adsorption isotherms for binary system (Ph-pnp) onto organoclay is shown in figure (3)

The parameters for each model were obtained using non-linear statistical fit of the equations to the experimental data .The Freundlich isotherm model was fitted with experimental data for each solute as a single , while for binary component systems the combination of Langmuir-Freundlich model was used. All parameters with correlation coefficients are summarized in Table 5.

From the figures and tables for single and binary component systems, It can be seen :

- equilibrium isotherm for each solute is of favourable type (i.e somewhat convex upward) and relatively high adsorbent loading were obtained at low concentrations of solute in water.
- The Freundlich model gives the best fit of the experimental data for single solute systems with high correlation coefficients. The equilibrium data for binary component systems were described successfully with Langmuir-Frendlich combination model for competitive adsorption.
- The q_e values for the binary systems were less than those in single systems due to competition between the solutes
- The constant parameters of the Freundlich model were found to be as (2.51 and 2.33) for n and as (0.314 and 0.559) for k for ph and pnp respectively .Where k is related primarily to the capacity of the adsorbent, and n is a function of the strength of adsorption. For fixed values of C_e and n the larger the value of k , the larger capacity (q_e). For fixed values of k and C_e, the smaller the value of n , the stronger the adsorption bond. The high value of k and the lower value of n indicated that the sorption capacity of organoclay for p-nitrophenol was very high compared with Phenol.
- Values of octanal-water coefficient (K_{ow}) (Table 1) shows that phenol is more hydrophilic than p-nitrophenol . This is due to the adverse effect of the OH group on adsorption of phenol,which may be attributed to the capability of this group to form hydrogen bonding with water and then renders the compound less liable to be adsorbed in comparison with pnp.
- The paranitrophenol is adsorbed to greater extent in comparison with phenol itself. This is attributed to the prevention of the formation of hydrogen bond either by forming an internal hydrogenbond between OH and the substitute group or by offering steric hinderance ,thereby increasing the solvophovic nature (i.e: decreasing solubility) as well as sorption capacity of the solute.
- The adsorption capacity can be compared for the three solutes in terms of (q_e). The maximum adsorptive capacities were (0.0.03 and 0.0344 kg/kg) for ph and pnp respectively, in which capacity order of pnp>Ph.
- There is a weak competition in binary systems in the adsorption capacity of solute in the presence of others , whereas the uptake of phenol is very much reduced by the presence of other solute .
- The competition between solutes in the binary solute systems reduced the sorbed amount of each solute compared with that in the single-solute system .

CONCLUSIONS

- Modification of natural clay to organoclay is resulting through the exchange of quaternary amine (hexadecyltrimethyl ammonium HDTMA$^+$) cation in place of Ca$^+$ at the surface of bentonite . This modification has been shown by different parameters. The CEC% for natural clay (80) increased to (136.71) for modified clay.The surface area decreased from 65 to 37.6 m^2 /g for natural and modified clay respectively.
- The order of adsorption capacity for binary systems onto organoclay are found to of pnp>ph. This order indicate that substituted phenols is adsorbed to greater extent in comparison with phenol itself.
- The competition between solutes in binary sorption systems caused reduction in the sorbed amount of each solute

compared with that in single solute system.

- The higher adsorption capacity of pnp onto organoclay may be explained by its lower solubility, higher molecular weight and higher octanal -water coefficient in comparison with phenol.

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List of Symbols

Symbols	**Descriptions**
b	Langmuir constant, m^3/kg
C_o	Initial concentration, kg/m^3
C_e	Equilibrium concentration, kg/m^3
F_{RP}	Radk-Prausnitz constant
k	Freundlich adsorption isotherm capacity constant,(mg/g,(mg/l)$^{-1/n}$
K_{RP}	Radk-Prausnitz constant
MW	Molecular weight
n	Freundlich adsorption isotherm intensity constant
N_{RP}	Radk-Prausnitz constant
Ph	Phenol
pnp	paranitrophenol
q_e	Internal concentration of solute in particle at equilibrium, kg/kg
q_m	Adsorption equilibrium constant defined by Lngmuir equation,kg/kg
R	Correlation coefficient
W	Weight of organoclay, kg

Table 1 Main properties of adsorbates used in this study [Agency for Toxic Substances and Disease Registry,1992]

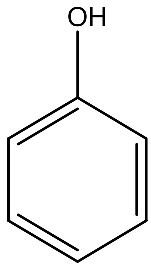
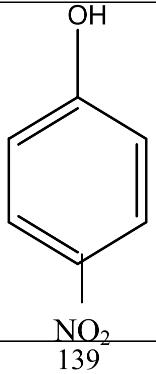
Property	**Phenol**	**Paranitrophenol**
Symbol	Ph	pnp
Formula	C_6H_5OH	$C_6H_5NO_3$
Structure		
Molecular weight, g/mole	94.11	139
Solubility in water (at 20° C), mg/l	86000	17000
Octanal-Water ,Log (K_{ow})	1.5	1.91
UV wave length (nm)	270	317

Table 2 Characteristics of powdered organoclay (Ibn Sina State Company and Ministry of oil)

Characteristic	**Value**		**Test Location**
	Bentonite	**Organoclay**	
Particle size,mm	0.075	0.75	University of Baghdad
Moisture content,%	7.2	0.36	Ibn Sina Company
Bulk density, kg/m^3	945	1025	Ibn Sina Company
Surface area, m^2/g	65	37.6	Ministry of oil
%CEC, meq/100g	80	136.72	University of Baghdad

Table 3 : Amine/100g bentonite as function of %CEC

%CEC	78.12	97.66	117.18	136.72	156.25	175.8	195.3
Amine/100g bentonite	20	25	30	35	40	45	50

Table 4 : Effect of different weight ratio of amine to bentonite on removal efficiency

Weight Ratio g	phenol C_o=50mg/l		p-nitrophenol C_o=50mg/l	
	Effluent Conc. mg/l	Removal %	Effluent Conc.mg/l	Removal %
20	34	32	30.2	39.6
25	25.8	48.4	21.6	56.8
30	17.2	65.6	13.7	72.6
35	8	84	5.8	88.4
40	10.1	79.8	7.75	84.5

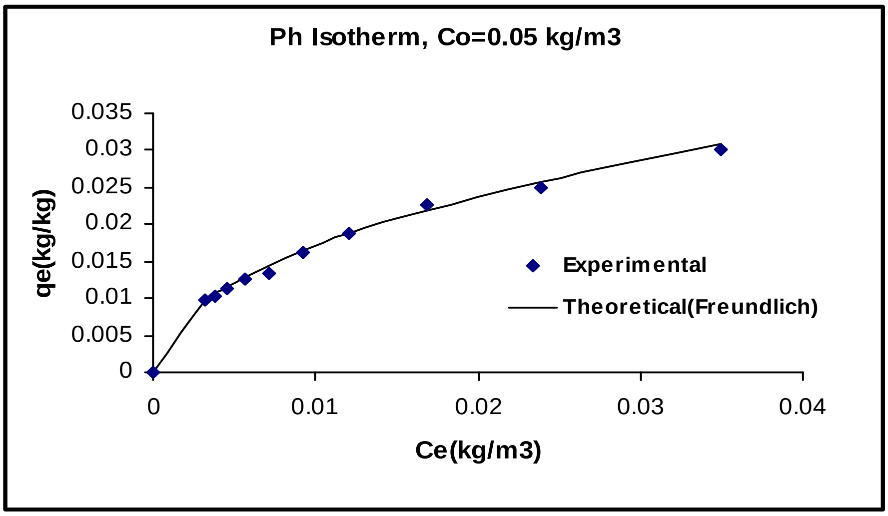


Fig. 1 : adsorption isotherm of phenol onto organoclay

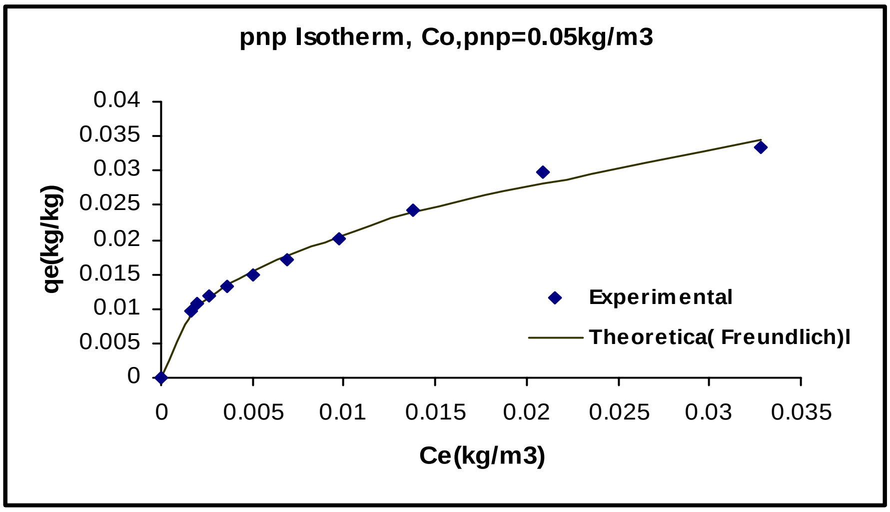


Fig. 2 : adsorption isotherm of p-nitrophenol onto organoclay

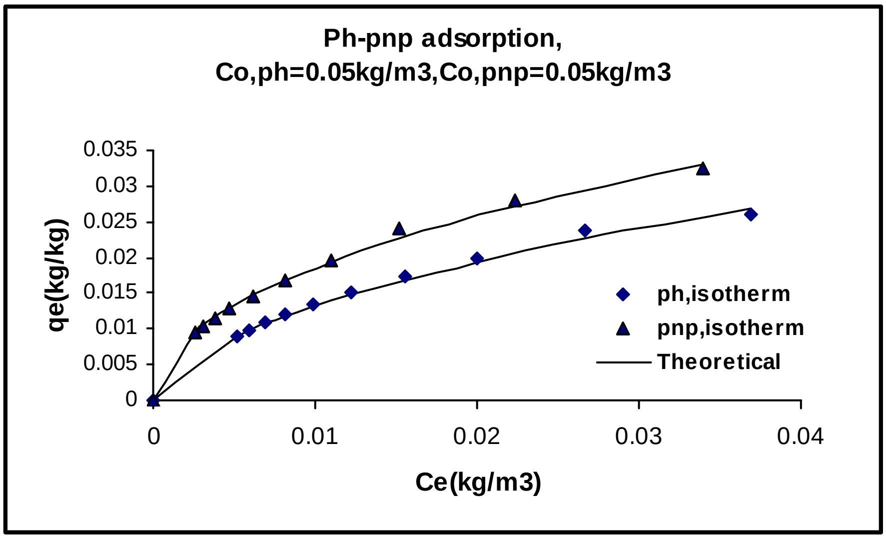


Fig. 3 adsorption isotherm of (Ph-pnp) as binary system onto organoclay

Table 5 :Parameters of single and binary system solutes isotherms for phenol and Paranitrophenol

Model	**parameters**	**phenol**	**p-nitrophenol**
Single Solute			
Freundlich Equation(4)	k	0.314	0.559
	n	2.51	2.33
	R^2	0.9990	0.9992
Langimur Equation(5)	q_m	0.397	0.391
	b	8.51	13.58
	R^2	0.9964	0.9831
Radk-Prausnitz Equation(6)	K_{RP}	15.95	22.15
	F_{RP}	0.48	0.56
	N_{RP}	0.4	0.43
	R^2	0.9942	0.9990
Binary system			
Model	parameters	Ph-pnp	
		Ph	pnp
Combination of Langimuir-Frendlich Equation(7)	q_m	0.391	0.384
	b	5.38	15
	n	1.87	0.577
	R^2	0.998	0.9932