

ADSORPTION EQUILIBRIUM OF PHENOLS FROM AQUEOUS SOLUTION USING MODIFIED CLAY

Hawaiah Imam Maarof, Bassim H. Hameed and Abdul Latif Ahmad
School of Chemical Engineering, Engineering Campus,
Universiti Sains Malaysia,
Seri Ampangan, Nibong Tebal, 14300 Seberang Perai Selatan,
Pulau Pinang, Malaysia.

Keywords: adsorption, Langmuir and Freundlich isotherms, o-cresol, phenol, 3-chlorophenol

ABSTRACT

The adsorption equilibrium study of phenol, 3-chlorophenol and o-cresol from liquid-phase system was carried out at temperature of 30°C using modified montmorillonite. A series of batch adsorption tests were carried out for various concentrations of phenols (25-200 mg/l) in a thermostatic shaker bath at agitation speed of 120 rpm. The single system adsorption process showed that the time required by the adsorbates to reach equilibrium conditions was about 2 hours under different initial concentrations. The results indicate that the percentage of removal at equilibrium for phenol, 3-chlorophenol and o-cresol were 70, 97 and 88%, respectively. The equilibrium data obtained for adsorption of phenol, 3-chlorophenol and o-cresol were well fitted to Freundlich isotherm model.

INTRODUCTION

Adsorption technology is prominent as the most effective method for removal of odor, oil, colours and trace amount of organic pollutants for purification of water and wastewater in industrial application. Literatures on the adsorption study of organic contaminants and dyes onto activated carbon are abundant (Tseng et al. 2003, Jung et al. 2001, Rajagopal & Kapoor 2001, Aksu & Yener 2001). Powdered and granular activated carbon has been proven as effective adsorbent in adsorption process. However, recently there have been attempts to exploit low cost material such as solid waste generate abundantly from industrial and natural occurring mineral sources in order to remove trace organic and inorganic contaminants from wastewaters due to the relatively high cost of activated carbons (Darwish et al. 1996, Aksu & Yener 2001).

In addition, there has been increasing interest in utilizing natural clay minerals like montmorillonite, kaolinite, sericite and illite for the removal of toxic metals, colors and some aromatic organic pollutants from aqueous solutions (Banat et al.

2000, Koh & Dixon 2001, Harris et al. 2002, Vengris et al. 2001). The abundance of natural clay in most continents of the world and its low cost make it a strong candidate as an adsorbent for the removal of many pollutants from wastewaters. Research studies have shown its ability to remove phenolic compounds and volatile organic compounds such as benzene and toluene (Koh & Dixon 2001). The adsorption behaviour was affected by several factors such as operating temperature, adsorption time, pH and pretreatment of the clay (Banat et al. 2000). Many investigations were carried out by other researchers on chemical treatment of mineral clay in order to enhance the adsorption capability using several modifying methods such as acid treatment and pillaring process (Koh & Dixon 2001, Wu et al. 2001, Lawrence et al. 1998). However, only limited studies were carried out to evaluate the adsorption equilibrium of phenolic compounds using natural or modified natural clay.

The objective of this research was to evaluate the equilibrium behaviour of liquid-phase adsorption of phenol and substituted phenol namely, 3-chlorophenol and o-cresol onto modified montmorillonite. Laboratory batch studies were conducted to estimate the adsorption capacity of the adsorbent for different adsorbate-adsorbent systems. The effect of contact time and initial concentration has been studied experimentally.

MATERIAL AND METHODS

The adsorbent was modified montmorillonite, supplied by Quicklab Sdn. Bhd. Ipoh, Malaysia and used without any further treatment. The modified montmorillonite was dried overnight in the oven at temperature of 60°C to remove any moisture content. Typical properties of the adsorbent were obtained from the supplier and other important properties were characterized for surface area and pore size using Autosorb I (Quantachrome Automated Gas Sorption System) supplied by Quantachrome Corporation, USA as shown in Table 1. Phenol (>99.5%), 3-chlorophenol (>90%) and o-cresol (99.5%) were purchased from Merck, Germany. Their physical properties are summarized in Table 2.

TABLE 1 Physical Properties of the Modified Montmorillonite

Properties	Value
Specific gravity	1.7
Color	Very light cream
Form	Finely Divided powder
Moisture content	2.0 %
Multi-point BET, m ² /g	13.15
Average pore diameter, nm	2.369

TABLE 2 Physical Properties of the Phenolic Compounds

Component	Phenol	3-Chlorophenol	O-cresol
Molecular Weight	94.11	128.56	108.13
Boiling Point	181.4 °C	214 °C	190.8 °C
Specific Gravity	1.071	1.268	1.048
Solubility* (H ₂ O)	8.2	2.6	2.5

* per 100 parts by weight of water (g/100g)

Adsorption Procedure

The aqueous stock solutions of phenol, 3-chlorophenol and o-cresol were prepared by dissolving a known amount of solid phenols with deionized water in the respective volumetric flasks. The stock solutions were then diluted to yield various desired concentrations of phenols in 250 ml volumetric flask. Batch mode laboratory test was conducted by adding a fixed amount of 2.5g of adsorbent to a series of 250 ml glass-stoppered flasks filled with 200 ml diluted solutions (25-200 mg/l). The glass-stoppered flasks were then placed in a thermostatic shaker bath at temperature of 30°C and agitated at 120 rpm until equilibrium condition was attained. Samples (4 ml) were taken at specify time intervals and filtered using GHP Acrodisc 0.45µm syringe filter to remove any remaining adsorbent in the solution. The concentrations of the liquid samples were then analyzed using Uv/Vis spectrophotometer (Shimadzu, UV-1601) at maximum wavelength of 270, 274.1 and 271.1 nm for phenol, 3-chlorophenol and o-cresol, respectively. The percentage amount of adsorbate adsorbed on the adsorbent was calculated by equation (1) where C_i and C_e are the initial and equilibrium concentrations of adsorbate, (mg/l).

$$\text{Percentage removal of the adsorbate} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

The amount of adsorbate adsorbed on modified montmorillonite was calculated according to the following equation:

$$q_e = \frac{V(C_o - C_e)}{W} \quad (2)$$

where C_o and C_e are initial and equilibrium liquid-concentration (mg/l), respectively, V is volume of solution (l) and W is weight of adsorbent (g).

RESULTS AND DISCUSSION

Effect of Time of Adsorption

The equilibrium times required for the adsorption of phenol, 3-chlorophenol and o-cresol were almost 2 hours as shown in Figures 1-3. However, the samples

were left overnight to assure that equilibrium condition was attained. Previous results on the adsorption kinetics of phenolics compounds using clay have shown a wide range of adsorption time. Wu et al. (2001) found that the adsorption time required to achieve equilibrium was about 20-90 minutes using an organic-montmorillonite, pillared montmorillonite and montmorillonite as adsorbents. In a separate study by Banat et al. (2000), and Viraraghavan & Alfaro et al. (1998), the equilibrium time for the adsorption of phenol on bentonite was 6 and 16 hours, respectively.

Figures 1-3 also show that the percentage of phenols removal for all initial concentrations studied at the equilibrium time was totally different for particular adsorbate-adsorbent system. The percentage of phenol, 3-chlorophenol and o-cresol removals on the adsorbent were 70%, 97% and 88%, respectively using different initial concentrations. The solubility of solute in the solvent/water has a significant effect on the adsorption process. The phenolic compounds studied have very fine molecular size, 0.8-1.0nm (Jung et al. 2001) but their solubility is absolutely different between each other. The solubility of phenol is infinitely higher than 3-chlorophenol and o-cresol (Table 2). The high solute polarity and its solubility decrease the tendency of adsorbate to adsorb from aqueous phase. The bonding between adsorbate and water must be broken before the adsorption process can be occurred (Weber Jr. 1985). Basically, greater solubility provides stronger bonding. Thus, phenol with the higher solubility compared to 3-chlorophenol and o-cresol has the lowest percentage of removal.

Effect of Initial Concentration

Figures 1-3 indicate that the amount of adsorbate adsorbed per unit weight of adsorbent increased with increasing of initial concentration. This means that an increase in initial adsorbate concentration resulted in increasing of solute uptake. The initial solute concentrations provide an importance driving force to overcome all mass transfer resistance of adsorbate between aqueous and solid phase. The higher initial solute concentration will decrease the mass transfer resistance. Hence, higher initial concentration of adsorbate enhances adsorption process with the result of higher interaction between solute and the adsorbent.

Adsorption Isotherm

Adsorption isotherm is useful to describe how solutes interact with adsorbents and very important to evaluate the feasibility of the adsorbate-adsorbent system. The isotherm data explained by theoretical or empirical equations provides preliminary prediction in modeling steps which is desired to practical operation. Adsorption isotherms of phenol, 3-chlorophenol and o-cresol onto modified montmorillonite are presented in Figure 4

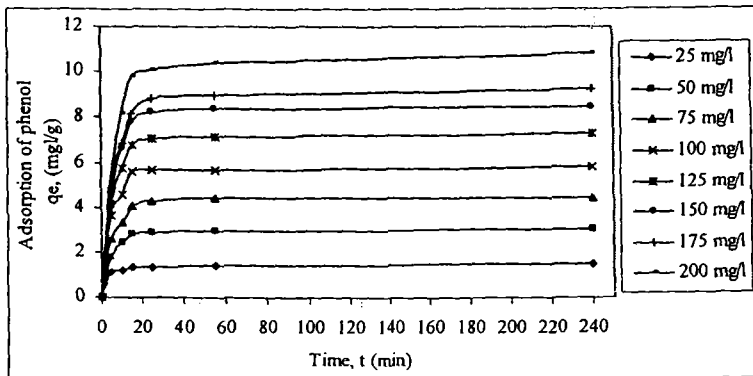


FIGURE 1 Phenol uptake by modified montmorillonite for different initial concentrations

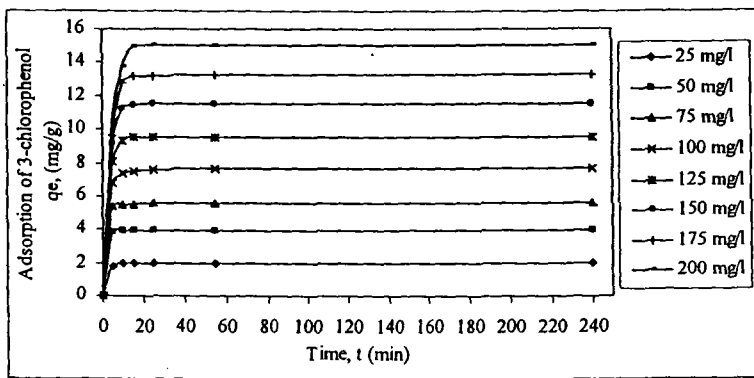


FIGURE 2 3-chlorophenol uptake by modified montmorillonite for different initial concentrations

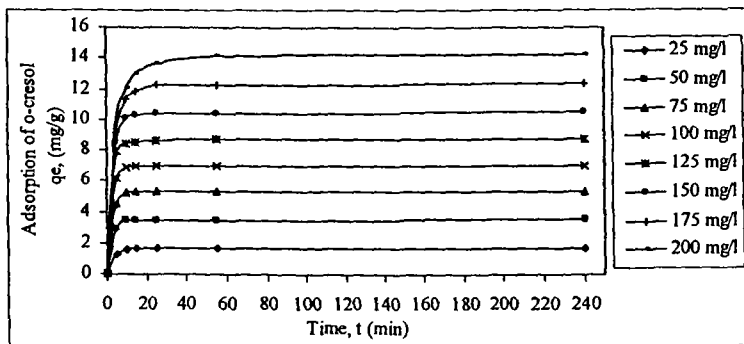


FIGURE 3 O-cresol uptake by modified montmorillonite for different initial concentrations

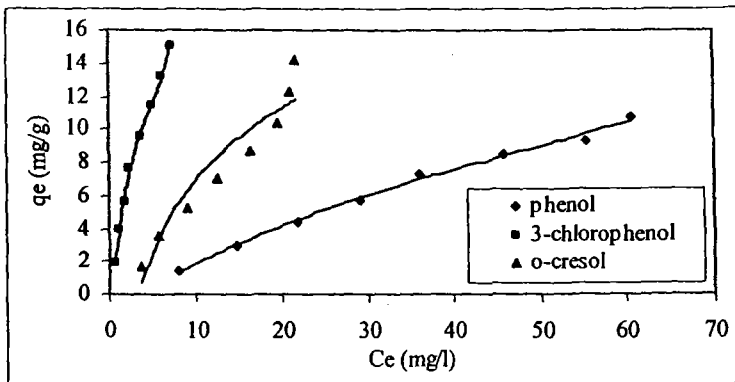


FIGURE 4 Adsorption isotherms of phenolic compounds using modified montmorillonite at temperature of 30°C

Langmuir Isotherm Model

The following relation can represent the linear form of the Langmuir isotherm model:

$$\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{bQ} \frac{1}{C_e} \quad (3)$$

where, q_e is the isotherm amount adsorbed at equilibrium (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l), and Q (mg/g) and b (l/mg) are the Langmuir constants related to the maximum adsorption capacity and the energy of adsorption, respectively. These constants can be evaluated from the intercept and the slope of the linear plot of experimental data of $1/q_e$ versus $1/C_e$ as shown in Figure 5.

Freundlich Isotherm Model

The linear form of the Freundlich isotherm model is given by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively of the sorbent.

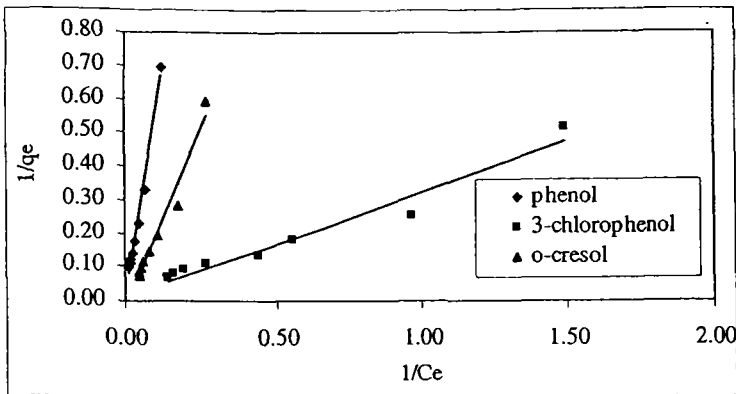


FIGURE 5 Langmuir isotherms for phenolic compounds adsorption on modified montmorillonite at temperature of 30°C

The values of K_F and $1/n$ can be obtained from the intercept and slope, respectively, of the linear plot of experimental data of $\log q_e$ versus $\log C_e$ as shown in Figure 6.

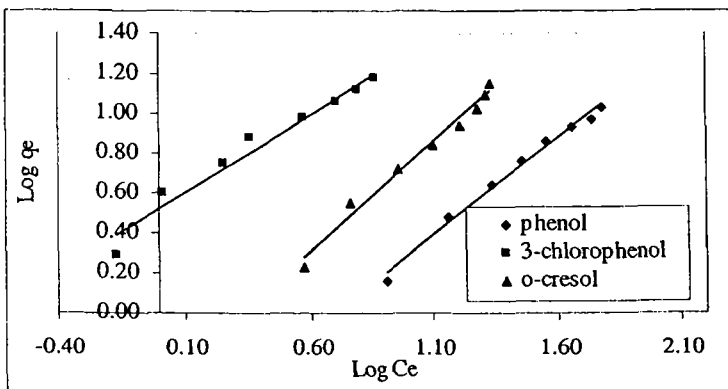


FIGURE 6 Freundlich isotherms for phenolic compounds adsorption on modified montmorillonite at temperature of 30°C

Values of Langmuir and Freundlich constants have been calculated from the plots in Figures 5 and 6, respectively and the results are tabulated in Table 3. The correlation coefficient, R^2 values, which are a measure of goodness-of-fit, show that both the Langmuir and Freundlich isotherm models can sufficiently, describes the adsorption data well for all three phenolic compounds studied. However, negative values for Langmuir isotherm constants for phenol and o-cresol adsorption are obtained. This indicates the inadequacy of the isotherm model to explain the adsorption process, since these constants are indicative of the surface binding energy and monolayer coverage. Thus adsorption of phenol,

3-chlorophenol and o-cresol can be very well described and fitted by Freundlich isotherm model. Similar finding was also reported by Wu et al. (2001).

TABLE 3 Langmuir and Freundlich constants for the adsorption of phenolic compounds onto modified montmorillonite at temperature of 30°C.

Component	Langmuir Isotherm Model			Freundlich Isotherm Model		
	Q*	b	R ²	K _F *	n	R ²
Phenol	-83.333	-0.002	0.99	0.2104	1.032	0.99
3-Chlorophenol	74.074	0.044	0.96	3.3458	1.270	0.97
O-cresol	-32.362	-0.014	0.97	0.4558	0.921	0.98

* units of Q and K_F were (mg/g) and (mg/g)(mg/l)ⁿ, respectively

The K_F in the Freundlich equation is related primarily to the capacity of the adsorbent for the adsorbate, and n is a function of the strength of adsorption. For fixed values of C_e and n, the larger the value of K_F, the larger capacity q. For fixed values of K_F and C_e, the smaller the value of n, the stronger is the adsorption bond. The fit of data to Freundlich isotherm model may indicate the heterogeneity of the adsorbed surface.

Brunauer, Emmett and Teller extended the Langmuir model to include multi-layer adsorption phenomena (Weber, Jr. 1985)

$$q_e = \frac{q_m K_{BET} X}{(1-X)[1 + (K_{BET} - 1)X]}$$

q_m is the amount of adsorption which takes place in a complete monolayer, K_{BET} is the constant expressive for the energy of adsorption and X=C_e/C_s (C_s is the saturation concentration of solute in water, which is temperature dependent). The values of q_m and K_{BET} can be obtained from the linearized plot of 1/[q_e(1-X)] versus (1-X)/X.

Component	BET Isotherm Model		
	q _m	K _{BET}	R ²
Phenol	-84.2799	-0.0054	0.9906
3-Chlorophenol	73.8951	0.0011	0.9617
O-cresol	-32.5275	-0.0028	0.9679

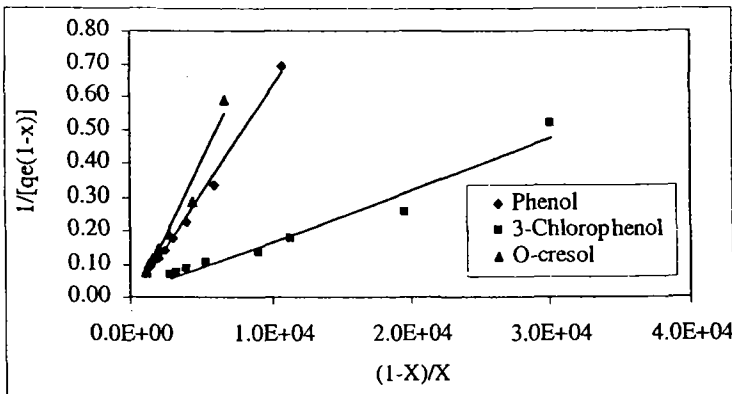


FIGURE 7 BET isotherms for phenolic compounds adsorption on modified montmorillonite at temperature of 30°C

The order of adsorption capacity among the phenolic compounds was 3-chlorophenol > o-cresol > phenol. The adsorption capacity of phenol has been found to be the lowest due to the effect of solute solubility as discussed above. However, this effect is not considerable to explain the adsorption capacity of 3-chlorophenol and o-cresol, as their solubility has no significant difference between each other.

CONCLUSION

Wastewaters containing phenolic compounds present a serious problem. Phenol-containing wastewater may not be conducted into open water without treatment because of toxicity of phenol. In this work, equilibrium studies were made for the adsorption of phenolic compounds from aqueous solutions onto modified montmorillonite in the concentration range (25-200 mg/l) at 30 °C. The results indicate that the percentage of removal at equilibrium for phenol, 3-chlorophenol and o-cresol were 70, 97 and 88%, respectively. The maximum adsorption capacity of modified montmorillonite was 0.508 for phenol, 1.670 for 3-chlorophenol and 0.710 for o-cresol. The affinity order was as follows:

3-chlorophenol > o-cresol > phenol. The equilibrium data obtained for adsorption of phenol, 3-chlorophenol and o-cresol were very well fitted to Freundlich isotherm model. The present work revealed that the adsorbent was promising material for the removal of phenol, 3-chlorophenol and o-cresol.

NOTATION

b	adsorption energy constant of Langmuir adsorption isotherm, (l/mg)
C_e	equilibrium liquid phase concentration, (mg/l)
C_o	initial liquid phase concentration, (mg/l)
K_{BET}	BET isotherm coefficient relating to adsorption energy
K_F	constant in Freundlich isotherm, (mg/g)(l/mg) ^{1/n}
n	Freundlich exponent
Q	the maximum surface coverage (formation of monolayer) of sorbent (mg/g)
q_e	equilibrium solid phase adsorbate concentration, (mg/g)
q_m	amount of adsorption, mg/g
R^2	correlation coefficient

REFERENCES

- Aksu, Z. and Yener, J. 2001. A Comparative Adsorption/biosorption Study of Mono-chlorinated Phenol onto Various Sorbents, *Waste Manag.*, **21**: 695-702.
- Banat, F.A., Al-Bashir, B., Al-Asheh, S. and Hayajneh, O. 2000. Adsorption of Phenol by Bentonite, *Env. Poll.*, **107**: 391-398.
- Jung, M. W., Ahn, K. H., Lee, Y., Kim, K. P., Rhee, J. S., Park, J. T. and Paeng, K. J. 2001. Adsorption Characteristics of Phenol and Chlorophenols on Granular Activated Carbon (GAC), *Microchem. J.*, **70**: 123-131.
- Darwish, N., Halhouli, K. and Al-Dhoon, N. 1996. Adsorption of Phenol from Aqueous Systems onto Spent Oil Shale, *Separation Scie. & Tech.*, **31**: 705-714.
- Koh, S. M. & Dixon, J. B. 2001. Preparation and Application of Organo-minerals as Sorbent of Phenol, Benzene and Toluene, *Applied Clay Sci.*, **18**: 111-122.
- Harris, R. G., Wells, J. D. and Johnson, B. B. 2002. Selective Adsorption of Dyes and Other Organic Molecules to Kaolinite and Oxide Surfaces, *Colloids and Surfaces, A: Physicochemical and Engineering Aspects.*, **180**: 131-140.
- Lawrence, M. A. M., Kukkadapu R. K. and Boyd S. A. 1998. Adsorption of Phenol and Chlorinated Phenols from Aqueous Solution by Tetramethylammonium- and Tetramethylphosphonium- exchanged Montmorillonite, *Applied Clay Scie.*, **13**: 13-20.
- Rajagopal, C. and Kapoor, J. C. 2001. Development of Adsorptive Removal Process for Treatment of Explosives Contaminated Wastewater using Activated Carbon, *J. Hazardous Material*, **B87**: 73-98.
- Tseng, R. L., Wu, F. C. and Juang, R. S. 2003. Liquid-phase Adsorption of Dyes and Phenols using Pinewood-based Activated Carbons, *Carbon*, **41**: 487-495.