[ENV03] Equilibrium adsorption study of 3-chlorophenol and o-cresol on modified montmorillonite

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Introduction

Phenolic compounds are commonly produced in wastewater streams generated by petrochemical, oil refineries, coal conversion, steel plant, paint and phenol-producing industries (Gallego et al., 2003; Aygün et al., 2003). The removal or destruction of phenolic compounds has become a significant environmental concern as less than 1 mg/L phenol is required for wastewater discharged, enacted Department of Environment (DOE) Malaysia in Environmental Quality Act 1979 (Sewage and Industrial Effluent). It is well known that phenolic compounds are toxic while some of these continents are carcinogenic. Numbers of conventional and recent technologies have leaded to propose various methods for treating wastewater containing phenolic compounds and its derivatives. The implementation of suitable method for removal of wastewater pollutant should be both environmentally acceptable and cost-effective. Adsorption process is a prominent method for removal of organic pollutants practically used by industries. Accordingly, abundantly reported findings were carried out on adsorption process using activated carbon. However, superior activated carbon is expensive and efforts to utilize low-cost adsorbent become a great intention. Thus, the aim of this study was to explore the potential of modified montmorillonite adsorbent for adsorption of 3-chlorophenol and o-cresol. The performance of modified montmorillonite was then compared with the commercial activated carbon, Norit 1240.

Materials and methods

Properties of adsorbent and adsorbates

The adsorbent was modified montmorillonite, supplied by Quicklab Sdn. Bhd. Ipoh, Malaysia and used without any further treatment. The commercial activated carbon, Norit 1240 was provided by Norit Nederland B.V., The Netherlands. Both adsorbents were dried overnight in an oven at temperature of 60^{o}C. 3-Chlorophenol (>95%) and o-cresol (99.5%) were purchased from Merck, Germany. Their physical properties are summarized in Table 1.

TABLE 1 Physical properties of the 3-chlorophenol (3CP) and o-cresol

Component	3CP	o-Cresol
Molecular Weight	128.56	108.13
Boiling Point (^{o}C)	214	190.8
Specific Gravity	1.268	1.048
Solubility* (H_2O)	2.6	2.5

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

Experimental procedure

Adsorption test was conducted using conventional batch system method. The stock of 1000 mg/L adsorbate solution was diluted to several different phenolic compounds concentrations ranging between 25 to 200 mg/L in volumetric flasks. A known amount of adsorbent was added to a series of 250 mL stoppered conical flasks filled with 200 mL diluted solutions. The glass-stoppered flasks were then placed in a water bath-shaker and shaken at agitation speed of 120 rpm and temperature of 30^{o}C. The samples were analyzed periodically using UV/Vis spectrophotometer (Shimadzu, UV-1601) to determine the remaining concentrations at maximum wavelengths of 274.1 and 271.1 nm for 3-chlorophenol and o-cresol, respectively. Shaking was continued until equilibrium condition was attained. 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) respectively.

$$\text{Percentage removal ,\%} = \frac{(C_i - C_e)}{C_i} x100 \quad (1)$$

While, the amount of solute adsorbed per unit weight of adsorbent (mg/g) was calculated according to the following equation (Denizli et al., 2005).

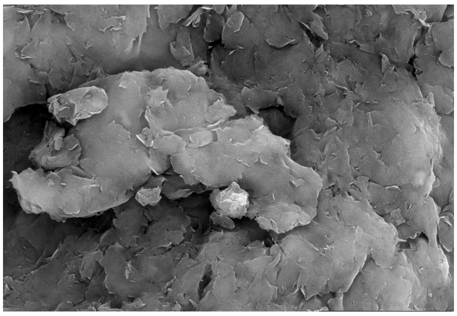
$$q_e = \frac{V(C_o - C_e)}{W} \quad (2)$$

Results and discussion

Characterization of adsorbents

Figures 1 (a) and (b) show the Scanning Electron Microscopy (SEM) images of modified montmorillonite and Norit 1240. Figure 1 (a) illustrates the irregular shapes of particles of powdered modified montmorillonite with the mean size around 2 to 3μm while Figure 1 (b) shows amorphous morphology of granular NAC 1240.

(a)



(b)

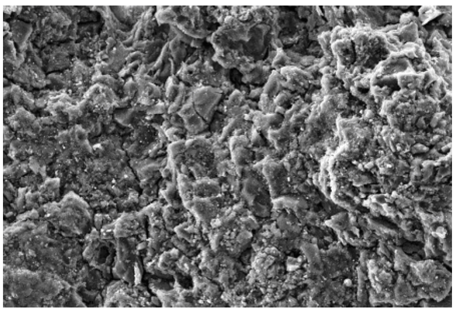


FIGURE 1 Scanning Electron Microscopy (SEM) images of (a) modified montmorillonite and (b) Norit 1240

It can be seen that the surface of Norit 1240 is rough. It presents a typical image of carboniferous material as reported by Jung et al. (2001). The characterization of adsorbents were carried out using Autosorb I (Quantachrome Automated Gas Sorption System) for their surface area and pore size properties, as shown in Table 2. Norit 1240 has significantly higher surface area than modified montmorillonite. While both adsorbents show almost similar values of average pore diameter within the range of mesopore adsorbent, which is appropriately good to be used for removal of organic pollutants in wastewater treatment system.

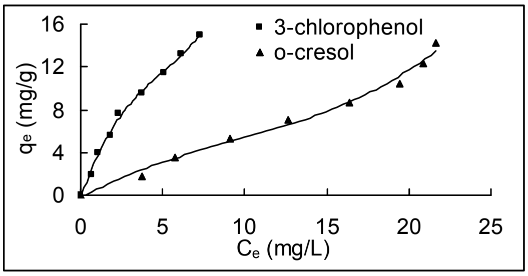
TABLE 2 Properties of the modified montmorillonite and Norit 1240

Properties	Value	
	Modified montmorillonite	**Norit 1240**
Multi-point BET, m^2/g	13.2	778.3
Average pore diameter, nm	2.37	2.72

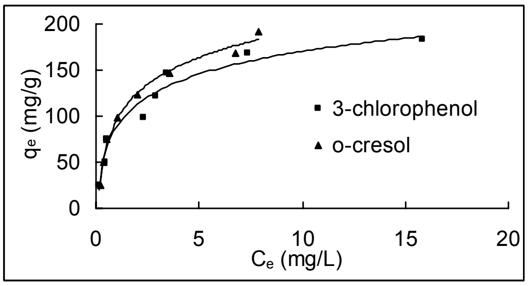
The compositions of modified montmorillonite are mainly Si and Al, a traditionally well known adsorbent. The presence of both SiO_2 and AlO_2 was determined by X-ray Fluorescence (XRF) spectrometry analysis and the amount of 55 wt% was obtained.

Adsorption equilibrium

Figures 2 (a) and (b) show the adsorption equilibrium of 3-chlorophenol and o-cresol using modified montmorillonite and Norit 1240 respectively. An amount of 2 g modified montmorillonite was used to adsorb different initial concentrations of 200 mL phenolic compounds solution. The results show that the equilibrium time required for the adsorption of 3-chlorophenol and o-cresol on modified montmorillonite were about 20 min and 25 min, respectively. However, the samples were left for 2 hours to assure that equilibrium condition was achieved.



(a) Modified montmorillonite



(b) Norit 1240

FIGURE 2 Adsorption equilibrium of 3-chlorophenol and o-cresol on (a) modified montmorillonite and (b) Norit 1240

The adsorption process on modified montmorillonite was considered fast because of a rapid increase of adsorbates adsorbed was occurred at the first 10 minutes. Previous findings on the adsorption of phenolic compounds by various clay-based adsorbents have shown a wide range of adsorption time. For example, Wu, et al. (2001) studied the adsorption of phenol on inorganic-organic pillared montmorillonite in polluted water. They reported that the adsorption time of phenol were 20, 30, and 90 min for organic-montmorillonite, pillared montmorillonite and montmorillonite, respectively. Therefore the result in this present study is in agreement with the other reported findings. Up to 97 and 88% of 3-chlorophenol and o-cresol, respectively were successfully adsorbed by modified montmorillonite from the aqueous solution. This proves the feasibility of modified montmorillonite as an effective adsorbent.

At equilibrium, it was observed that 3-chlorophenol (97%) gives higher percentage removal than o-cresol (88%). It could be interpreted based on the interaction between adsorbate and adsorbent. The adsorption of phenolic compounds on adsorbent may involve electron donor-acceptor complexes or may imply dispersion forces between π-electron in adsorbate and adsorbent (Jung et al., 2001). The chloro group is an electron-withdrawing group and therefore, the electron density in aromatic ring of 3-chlorophenol is lower than o-cresol. As a result, 3-chlorophenol showed the highest affinity to the π-electron of double bonds in modified montmorillonite which contributed to greater amount of percentage removal of 3-chlorophenol than o-cresol.

On the other hands, the amount of adsorbates adsorbed on Norit 1240 was higher than the adsorption on modified montmorillonite as illustrates by Figure 2 (b). However, the equilibrium time for adsorption of 3-chlorophenol and o-cresol on Norit 1240 was about 24 hours and the percentage removal was 92% for both adsorbates.

Adsorption isotherm

(a) Langmuir Isotherm Model

Langmuir model assumes that the adsorption energy is constant and independent of surface coverage, adsorption occurs on localized sites with no interaction between adsorbate molecules and maximum adsorption occurs when the surface is covered by a monolayer of adsorbate (Langmuir, 1918). The following relation represents 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 3.

(b) Freundlich Isotherm Model

Freundlich model is predicated based on the assumption that maximum adsorption capacity consists of a monolayer adsorption. It occupied heterogeneous adsorption surface and active sites with different energy which is unlike the Langmuir model. The linear form of the Freundlich isotherm model is given by the following equation (Freundlich, 1926):

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

where K_F and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, respectively of the sorbent. 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 4.

Based on values of correlation coefficient, R^2 summarized in Table 3, the adsorption of 3-chlorophenol on modified montmorillonite was described well by both Langmuir and Freundlich models. Both homogeneous and heterogeneous adsorption energy took place during the process. On the other hand, the negative value of the Langmuir constant, Q (mg/g) for o-cresol adsorption indicates an inadequacy of the Langmuir model to explain the process. Thus, Freundlich model was the best model to explain the adsorption behavior of o-cresol on modified montmorillonite.

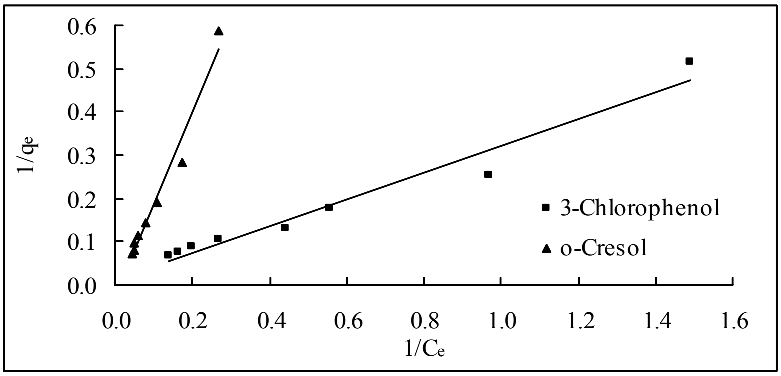


FIGURE 3 Langmuir isotherms for 3-chlorophenol and o-cresol adsorption on modified montmorillonite at temperature of 30°C

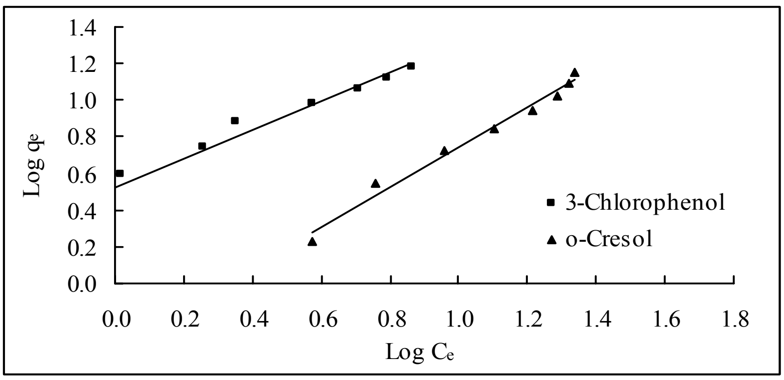


FIGURE 4 Freundlich isotherms for 3-chlorophenol and o-cresol adsorption on modified montmorillonite at temperature of 30°C

TABLE 3 Adsorption constants for adsorption of 3-chlorophenol and o-cresol on modified montmorillonite and Norit 1240

	Langmuir Isotherm Model			Freundlich Isotherm Model		
	Q*	b	R^2	K_F*	n	R^2
Modified montmorillonite						
3-Chlorophenol	74.1	0.04	0.96	3.35	1.27	0.97
o-Cresol	-32.4	-0.01	0.97	0.46	0.92	0.98
Norit 1240						
3-Chlorophenol	200.0	0.70	0.99	72.3	2.38	0.92
o-Cresol	212.8	0.77	0.99	78.9	2.10	0.90

* units of Q and K_F were (mg/g) and $(mg/g)(L/mg)^{1/n}$, respectively

For comparison, the parameter constants for adsorption of 3-chlorophenol and o-cresol on Norit 1240 are also listed in Table 3. Based on values of correlation coefficient, R^2, the adsorption of 3-chlorophenol and o-cresol were best fitted by Langmuir model. In addition, it is clearly seen that the adsorption capacity, Q (mg/g) for adsorption of 3-chlorophenol on Norit 1240 was significantly higher than adsorption on modified montmorillonite. Besides, the values of Freundlich constant K_F which has been taken as an indicator of adsorption capacity, was also greater for adsorption of o-cresol on Norit 1240 as compared to the adsorption on modified montmorillonite. However, modified montmorillonite still shows its feasibility and is a promising adsorbent since it is abundantly available and cheaper than commercial activated carbon. Basically, a good adsorption by Norit 1240 could be explained by its high surface area while the feasibility of modified montmorillonite was contributed by its chemical properties which was mainly consists of Si and Al. Additionally, the presents study proved that the adsorption of 3-chlorophenol on modified montmorillonite was higher than the result obtained by Lin and Ching (2002). They reported that only 0.64 $(mg/g)(L/mg)^{1/n}$ of K_F value was determined for adsorption of 3-chlorophenol on organobentonite.

Conclusion

Modified montmorillonite was a potential and promising adsorbent for removal of phenolic compounds from aqueous solution. The results were compared with commercial activated carbon, Norit 1240. The adsorption of 3-chlorophenol and o-cresol on Norit 1240 were higher than adsorption on modified montmorillonite. However, modified montmorillonite stand as low-cost adsorbent and its shows the feasibility to remove up to 97 and 88% of 3-chlorophenol and o-cresol, respectively for initial concentration between 25-200 mg/L.

Acknowledgements

The authors acknowledge the research grant provided by Universiti Sains Malaysia, Penang that has resulted in this article. Sincere gratitude to Ministry of Science Technology and Innovation (MOSTI) for National Science Fellowship awarded to Hawaiah Imam Maarof.

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