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Adsorption of phenol from wastewater by organo-bentonite

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ABSTRACT

Na–bentonite was modified via an ion-exchange reaction with hexadecyl trimethyl ammonium bromide (CTAB). X-ray diffractometer (XRD) indicated CTAB cations had exchanged with Na^+ ions in Na–bentonite and the interlayer space of bentonite was increased. Batch adsorption tests were carried out to remove phenol from model wastewater using the modified bentonite, and the effect of amount of CTAB, contact time, pH, and adding quantity of modified bentonite were evaluated. The experimental results showed that the removal efficiency of phenol can be up to 81.36% under the following conditions: the amount of CTAB was 1.5 cation exchange capacity (CEC), the dosage of organic modified bentonite was 7 g/L, the adsorption time was 60 min, and the pH value was 7. The adsorption isotherms of organic modified bentonite for phenol-based wastewater met the Freundlich adsorption equation.

Keywords: Bentonite; Phenol; Adsorption; Hexadecyl trimethyl ammonium bromide (CTAB); Wastewater

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1. Introduction

The rapid development of chemical and petrochemical industries over the past several decades has caused public concern about the widespread contamination of waters by various organic compounds which are generated during the manufacturing and processing stages of organic chemicals. The organic contents in these wastewaters usually exceed the level for safe discharge. Phenols are common contaminants in wastewater generated from petroleum and petrochemicals, coal conversion, phenol-producing industries, and plants which are processing phenols to plastics [1,2]. Phenol is considered as a priority pollutant in wastewaters as it is highly toxic to organisms even at low concentrations and has been classified as a hazardous pollutant because of its potential harm to human health [3]. Therefore, the removal of phenol from the wastewater has become an integral part of wastewater treatment systems in the chemical and petrochemical industries.

There are many methods for the removal of phenol from wastewater such as microbial degradation, chemical oxidation, photocatalytic degradation, solvent extraction, adsorption, and membrane processes [4–14]. Adsorption is the most popular method in which activated carbon, macroporous resin, or layered silicate clay are usually used. Activated carbons and macroporous resin have the advantage of high adsorp-

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tion capacity for phenolic compounds. However, their relatively high costs make them less economically viable as an adsorbent and limit them of industrial applications. There have been attempts to utilize low-cost, natural adsorbents to remove trace organic and inorganic contaminants from wastewaters [15].

The abundance of bentonite in most continents of the World and its low cost makes it a strong candidate as an adsorbent for the removal of many pollutants from wastewaters [1,16]. Natural bentonite is not efficient as an adsorbent for the uptake of hydrophobic organic pollutants from aqueous solution primarily due to the electrically charged and hydrophilic characteristics of its surface [17]. But organo-bentonites which are produced by replacing exchangeable inorganic cations (e.g. Na^+, Ca^{2+}, H^+) on the internal and external mineral surfaces of bentonite with quaternary alkyl ammonium cations have enhanced sorption capacities for nonionic organic pollutants [18,19].

Due to unique sorption capabilities of organo-bentonite, it has been of considerable interest in applying it to adsorb organic substances from wastewaters. In this paper, hexadecyl trimethyl ammonium bromide (CTAB) was used to prepare organo-bentonite and the adsorption properties of organo-bentonites to phenol in model wastewater were investigated in detail.

2. Materials and methods

2.1. Materials

The natural bentonite was obtained from Jianping County, LiaoNing Province, China. The bentonite was industrial grade. Its chemical composition is shown in Table 1 and the cation exchange capacity (CEC) was 71.39 mmol/100 g. Coarse fraction impurities were removed by subjecting the bentonite dispersions to repeated sedimentation. The layer at the bottom was removed and upper portions were exposed to sedimentation until no gritty layer remained. After drying at 60℃, the sample was pulverized to pass through 120 standard mesh.

Table 1
Chemical composition of bentonite (%)

Al_2O_3	16.05
SiO_2	59.82
MgO	3.64
Fe_2O_3	6.55
Na_2O	3.62
K_2O	0.84
CaO	0.91
TiO_2	0.72
MnO	0.07

CTAB and phenol were analytical reagent grade and used without further purification. A solution containing phenol was prepared by dissolving a known amount of phenol in deionized water to the desired concentrations (50 mg/L). The pH of the solution was adjusted using 0.1 mol/L NaOH or HCl.

2.2. Organo-bentonite preparation

One gram of pretreated bentonite was placed in 250 ml conical flask and an appropriate amount of distilled water was added. The system was subjected to a mechanical stirring in warm water bath and heated up to 60℃, then solutions containing CTAB were added under stirring for 30 min at 60℃, after that it was taken out from the warm water bath to cool to ambient temperature and allowed to stand for 24 h. Bentonite was then separated from the solution via centrifugation, washed twice with distilled water, and dried at 80℃. This bentonite is designated as organo-bentonite. The dry organo-bentonite was ground to less than 120 standard mesh and then stored for further use in the adsorption tests.

2.3. Characterization of organo-bentonite

X-ray diffractometer (XRD) patterns were obtained by a Rigaku D/Max-3c X-ray diffractometer using monochromatised-Cu/K radiation (40 kV, 40 mA). The samples were scanned using a step size of 4° (2θ) per min.

2.4. Batch adsorption experiments

Batch adsorption experiments were carried out in a group of 250 ml stoppered conical flasks which contained 100 ml solution of known concentration of phenol and the pH was adjusted using dilute HCl or NaOH solutions. Subsequently, an accurately weighted amount of organo-bentonite was added to them and agitated on a constant temperature oscillator at a given temperature for regular time. After centrifuging, the phenol concentration of the supernatant was measured using a 4-amidoantipyrine spectrophotometer method and then the removal efficiency of phenol in water was calculated.

3. Results and discussion

3.1. Effect of the amount of CTAB on adsorption of phenol by organo-bentonite

The effects of CTAB were examined in more detail in the following series of experiments, wherein the amounts of the organo-bentonite (0.5 g), pH (6), temperature (25℃), and adsorption time (60 min) were kept constant, while the contents of CTAB varied (0.5 CEC, 1.0 CEC, 1.5 CEC, 2.0 CEC, respectively). XRD patterns of bentonite and organo-bentonite are shown in Fig. 1.

Fig. 1 shows that the basal spacing of Na- bentonite is 1.26 nm. After the modification process, this basal spacing is increased to 2.1 nm or so. It means that the CTAB cations were intercalated in the interlayer space of the bentonite. With the insertion of cethyl ammonium cation into the bentonite interlayer, the bentonite becomes hydrophobic.

Because the CEC of bentonite in the experiment is 71.39 mmol/100 g, it shows that 100 g bentonite can react with 71.39 mmol CTAB completely under ideal status in which the organic quaternary ammonium cation (CTAB) has completely intercalated into the layers of bentonite. However, in practice, the ideal status cannot be attained, so the method of increasing the dosage of quaternary ammonium salt was applied to prompt the bentonite intercalated reaction. As you can see in Fig. 1, the spacing increased gradually with CTAB, when the contents of CTAB over the 1.5 CEC of the initial bentonite, the interlayer spacing of organo-bentonite did not increase further. The results were identical with those reported in literature [20].

The dependency of the phenol adsorption with the contents of CTAB is shown in Fig. 2. As can be seen, the presence of cationic surfactants (CTAB) exhibited a rather pronounced effect on the adsorption of phenol on bentonite. As CTAB concentration added up to 1.5 CEC, the adsorption percentage of phenol reached the highest and it corresponded to the capacious interlayer spacing of organo-bentonite (Fig. 1). So, the suitable dosage of CTAB was 1.5 CEC of the initial bentonite.

3.2. The effects of pH on phenol removal efficiency

100 ml solutions of 50 mg/L of phenol were placed in a group of 250 ml stoppered conical flask and 0.5 g of organo-bentonite was added to these conical flasks. Then, the pH was adjusted ranging from 4 to 8, respectively. They were agitated on a constant temperature oscillator for 60 min at 25℃ and centrifuged at 1,500 rpm for 10 min. The removal of the adsorbed phenol was calculated. The effect of solution pH on the adsorption of phenol by organo-bentonite is shown in Fig. 3.

Fig. 3 shows that the best adsorption efficiency on organo-bentonite to phenol was achieved at the pH 6–7, while at pH less than 6 or higher than 8, the adsorption efficiency decreased. This phenomenon could be explained as the dependency of phenol ionization on the different pH values. H^+ in the solution could exchange quaternary ammonium cations existing in the layers of organo-bentonite to a certain degree under acidic conditions ($pH < 6$), which contributed to a part of organo-bentonite degeneration, and it resulted in the decrease of oleophylic and hydrophobic property of organo-bentonite leading to the decrease of the adsorptive capacity of organo-bentonite to phenol. While phenol existed in solution as neutral molecule C_6H_5OH under netural conditions, it was easily adsorbed by hydrophobic bond of alkyl organic phase of organo-bentonite, hence the adsorbability of organo-bentonite to phenol would increase. While phenol existed in solu-

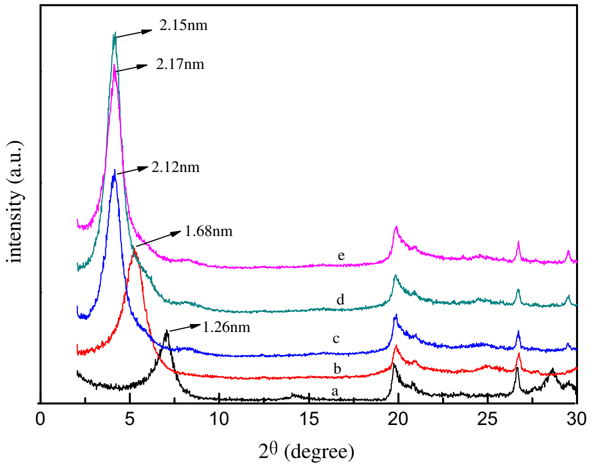

Fig. 1. The XRD patterns (a) bentonite, (b) 0.5 CEC CTAB-bentonite, (c) 1.0 CEC CTAB-bentonite, (d) 1.5 CEC CTAB-bentonite, and (e) 2.0 CEC CTAB-bentonite.

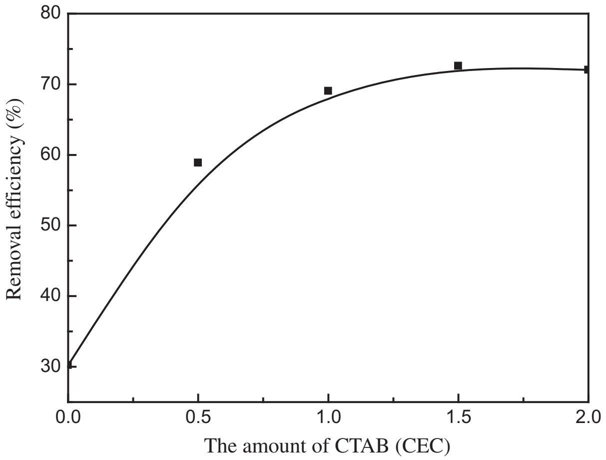

Fig. 2. Effect of amount of CTAB on adsorption of phenol.

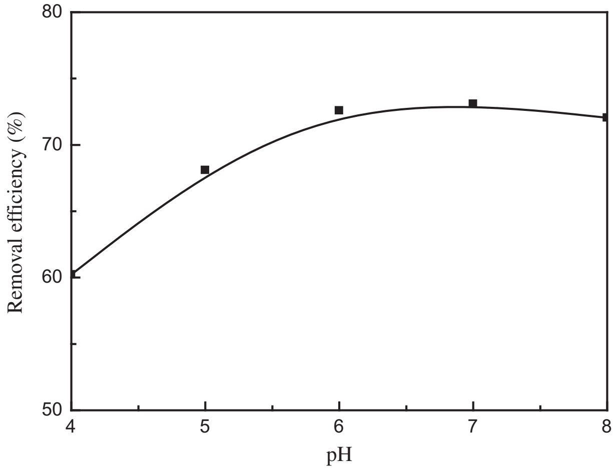

Fig. 3. Effect of pH on phenol removal efficiency.

tion as negative ion $C_6H_5O^-$ in basic conditions, its solubility in water was relatively high, meanwhile it repelled with negative charges of organo-bentonite layers, and caused adsorptive capacity of organo-bentonite on phenol to decrease. So the appropriate pH was 6–7. In the follow-up experiment, pH was kept 7.

3.3. The effects of organo-bentonite dose on phenol removal efficiency

In order to investigate the effects of organo-bentonite dose on phenol removal efficiency, 100 ml solutions of 50 mg/L of phenol were placed in a group of 250 ml stoppered conical flask, adjusting pH to 7 with either 0.1 M HCl or 0.1 M NaOH. Then 0.3, 0.4, 0.5, 0.6, 0.7, and 0.8 g of organo-bentonite were added to conical flask, respectively (i.e. organo-bentonite dose was 3, 4, 5, 6, 7, and 8 g/L). They were agitated on a constant temperature oscillator for 60 min at 25℃ and centrifuged at 1,500 rpm for 10 min. The removal of the adsorbed phenol was calculated. The effect of organo-bentonite dose on the removal of phenol is illustrated in Fig. 4.

From Fig. 4, we can see the adsorption of organo-bentonite to phenol enhanced obviously and that the phenol removal efficiency increased significantly with the increase in organo-bentonite dose, and phenol removal efficiency increased from 60.17 to 81.95% as the organo-bentonite dose was increased from 0.3 to 0.8 g (i.e. from 3 to 8 g/L). The increased removal of phenol with increasing organo-bentonite dose could be due to the increased absolute adsorption surface. When organo-bentonite dose was about 0.7 g (i.e. 7 g/L), the removal efficiency was 81.36%, which was nearly close to maximized value. However, the removal efficiency increased much slower when the organo-bentonite dose was over 0.7 g (i.e. 7 g/L) because the adsorption was nearly saturated. So the appropriate dosage of organo-bentonite is 7 g/L for phenol wastewater at a concentration of 50 mg phenol/L. At this point, the adsorption capacity of organo-bentonite is 5.8 mg phenol/g organo-bentonite.

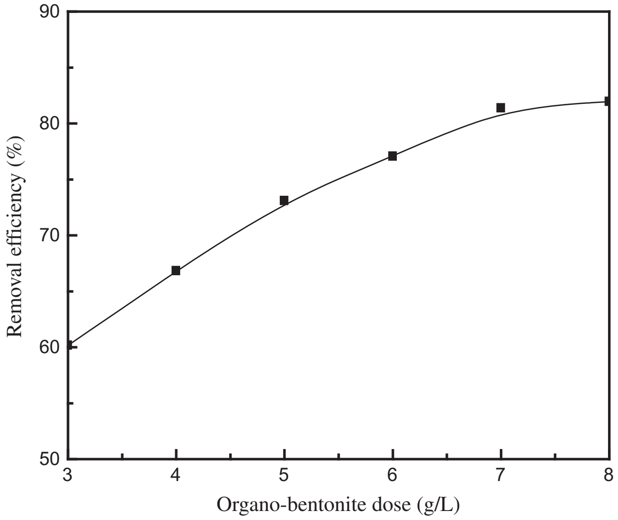

Fig. 4. Effect of organo-bentonite dose on phenol removal efficiency.

3.4. The effect of agitation time on phenol removal efficiency

To know the influence of the adsorption time, 100 ml solutions of 50 mg/L of phenol were adjusted to pH 7 with either 0.1 M HCl or 0.1 M NaOH. Then 0.7 g of organo-bentonite was added to the conical flask. They were agitated on a constant temperature oscillator for different time-spans at 25 ℃ and centrifuged at 1,500 rpm for 10 min. The adsorption data for the uptake of phenol vs. agitation time is presented in Fig. 5.

As seen from Fig. 5, the phenol removal efficiency increased with increase in agitation time till the agitation time reached 60 min. The phenol removal efficiency was found to be 81.36% at 60 min. After 60 min, the amount of phenol adsorbed remained almost the same and the curve of the removal efficiency became parallel to the time axis. According to these results, the 60 min agitation time was considered to be sufficient for the adsorption of phenol onto organo-bentonite.

3.5. Adsorption isotherms of phenol

Phenol adsorption isotherms from aqueous solutions were obtained using the batch equilibration technique. Various amounts of adsorbent (0.3, 0.4, 0.5, 0.6,

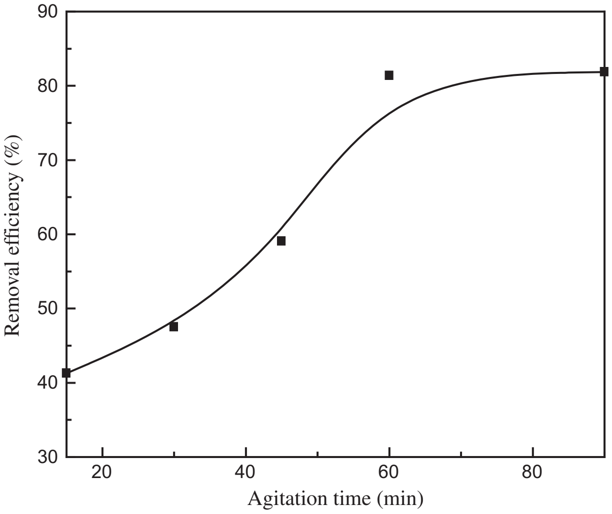

Fig. 5. Effect of agitation time on phenol removal efficiency.

and 0.7 g) were added to 100 ml of 50 mg/L of phenol solutions and the value of pH was adjusted to 7 with either 0.1 M HCl or 0.1 M NaOH. They were agitated on a constant temperature oscillator for 60 min at 25℃ and centrifuged at 1,500 rpm for 10 min. The phenol concentration of the supernatant was measured using a 4-amidoantipyrine spectrophotometer method.

Freundlich isotherm is used for modeling the adsorption on heterogeneous surfaces. Freundlich isotherm can be defined according to the following formula:

$$q_e = K_F c_e^{1/n}$$

where q_e is the amount adsorbed at equilibrium (mg/g) and c_e is the equilibrium concentration (mg/L). K_F and n are equilibrium constants indicative of adsorption capacity and adsorption intensity, respectively.

The logarithmic linear form of the Freundlich equation is given as:

$$\lg q_e = 1/n \lg c_e + \lg K_F$$

In this work, the Freundilich isotherm models were used to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solutions.

Fig. 6 shows the dependence of $\lg q_e$ on $\lg c_e$, and K_F and $1/n$ were calculated from the intercept and slope of the plot of $\lg q_e$ vs. $\lg c_e$.

As shown in Fig. 6, the Freundlich equation fitted fairly well to the experimental data. The correlation coefficient value was found to be 0.993. The results are similar to those reported previously [1]. The regression equation is as follows: $\lg q_e = 0.71 \lg c_e + 0.059$. So the parameters, K_F and $1/n$, were found to be 1.15 and 0.71, respectively. These values show that the capacity of adsorbent is high.

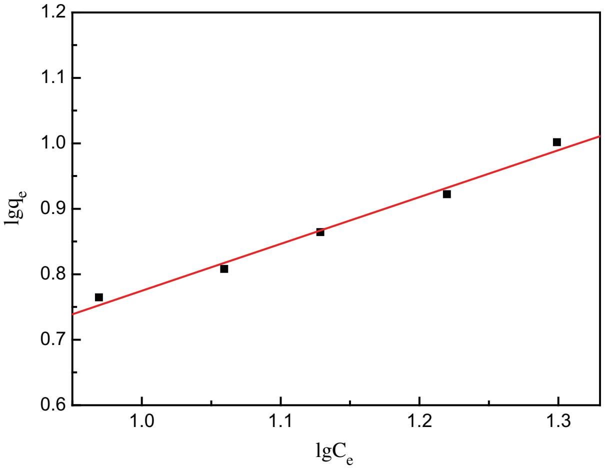

Fig. 6. Freundlich adsorption isotherms on organo-bentonites.

4. Conclusions

The organo-bentonite adsorbents were successfully prepared with cation exchange reaction between Na–bentonite and the CTAB. And, the CTAB cations were intercalated in the interlayer space of the bentonite. The satisfying adsorption efficiency to phenol was achieved using organo-bentonite as adsorbents with adsorption time of 60 min, initial phenol solution pH 7, organo-bentonite dosage 7 g/L, and 25℃. Adsorption isotherms of phenol on organo-bentonite belonged to Freundlich model. The adsorption isotherm could be described as $q_e = 1.15c_e^{0.71}$.

References

[1] S. Al-Asheh, F. Banat, L. Abu-Aitah, Adsorption of phenol using different types of activated bentonites, Sep. Purif. Technol. 33 (2003) 1–10.

[2] F.A. Banat, B. Al-Bashir, S. Al-Asheh, O. Hayajneh, Adsorption of phenol by bentonite, Environ. Pollut. 107 (2000) 391–398.

[3] Y. Huang, X. Ma, G. Liang, H. Yan, Adsorption of phenol with modified rectorite from aqueous solution, Chem. Eng. J. 141 (2008) 1–8.

[4] M. Shourian, K. Noghabi, H. Zahiri, T. Bagheri, G. Karballaei, M. Mollaei, I. Rad, S. Ahadi, J. Raheb, H. Abbasi, Efficient phenol degradation by a newly characterized *Pseudomonas* sp. SA01 isolated from pharmaceutical wastewaters, Desalination 246 (2009) 577–594.

[5] P. Saravanan, K. Pakshirajan, P. Saha, Biodegradation kinetics of phenol by predominantly *Pseudomonas* sp. in a batch shake flask, Desalin. Water Treat. 36 (2011) 99–104.

[6] Y. Wang, B. Gu, W. Xu, Electro-catalytic degradation of phenol on several metaloxide anodes, J. Hazard. Mater. 162 (2009) 1159–1164.

[7] C. Yang, Y. Qian, L. Zhang, J. Feng, Solvent extraction process development and on-site trial-plant for phenol removal from industrial coal-gasification wastewater, Chem. Eng. J. 117 (2006) 179–185.

[8] W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capala, I. Ostrowska, Removal of phenol from wastewater by different separation techniques, Desalination 163 (2004) 287–296.

[9] K.P. Singh, A. Malik, S. Sinha, P. Ojha, Liquid-phase adsorption of phenols using activated carbons derived from agricultural waste material, J. Hazard. Mater. 150 (2008) 626–641.

[10] H. Cherifi, S. Hanini, F. Bentahar, Adsorption of phenol from wastewater using vegetal cords as a new adsorbent, Desalination 244 (2009) 177–187.

[11] G. Busca, S. Berardinelli, C. Resini, L. Arrighi, Technologies for the removal of phenol from fluid streams: A short review of recent developments, J. Hazard. Mater. 160 (2008) 265–288.

[12] W. Kujawski, A. Warszawski, W. Ratajczak, T. Porebski, W. Capała, I. Ostrowska, Application of pervaporation and adsorption to the phenol removal from wastewater, Sep. Purif. Technol. 40 (2004) 123–132.

[13] Y. Li, J. Wei, C. Wang, W. Wang, Comparison of phenol removal in synthetic wastewater by NF or RO membranes, Desalin. Water Treat. 22 (2010) 211–219.

[14] H. Koseoglu, B.I. Harman, N.O. Yigit, N. Kabay, M. Kitis, The impacts of operational conditions on phenol removal by nanofiltration membranes, Desalin. Water Treat. 26 (2011) 118–123.

[15] M.H. El-Naas, S. Al-Zuhair, M.A. Alhaija, Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon, Chem. Eng. J. 162 (2010) 997–1005.

[16] M. Hermosin, P. Martin, J. Cornej, Adsorption mechanisms of monobutyltin in clay minerals, J. Environ. Sci. Technol. 27 (1993) 2606–2611.

[17] S. Yapar, V. Ozbudak, A. Dias, A. Lopes, Effect of adsorbent concentration to the adsorption of phenol on hexadecyl trimethyl ammonium-bentonite, J. Hazard. Mater. 121 (2005) 135–139.

[18] S.H. Lin, M.J. Cheng, Adsorption of phenol and m-chlorophenol on organobentonites and repeated thermal regeneration, Waste Manage. 22 (2002) 595–603.

[19] Z. Li, R.S. Bowman, Counter ion effects on the sorption of cationic surfactant and chromate on natural clinoptiloite, Environ. Sci. Techonol. 31 (1997) 2407–2412.

[20] A. Khenifi, B. Zohra, B. Kahina, H. Houari, D. Zoubir, Removal of 2,4-DCP from wastewater by CTAB/bentonite using one-step and two-step methods: A comparative study, Chem. Eng. J. 146 (2009) 345–354.