An Investigation of Phenol Adsorption from Aqueous Solution Using Solid Adsorbents

Wilaiporn Insuwan* and Nantana Saosai

Faculty of Agriculture and Technology, Rajamangala University of Technology Isan, Surin Campus, Surin 32000, Thailand

* Corresponding author. E-mail address: wi_insuwan@hotmail.com

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Abstract

This study reports on removal of phenol on various solid adsorbents namely, activated carbon (AC), zeolite LTL in 2 forms, K-LTL and H-LTL. This work was performed by batch adsorption techniques. The effect of adsorbent, pH and temperature were determined to find out the optimal condition. The amounts of adsorbed phenol were interpreted using Langmuir and Freundlich. K-LTL zeolite was found to be most effective for the removal of phenol than H-LTL and AC. The optimum conditions for maximum adsorption were K-LTL being used as an adsorbent, at pH 4. Moreover, it was found that the adsorption was enhanced with increasing temperature. This results showed that the K-LTL zeolite exhibit a better an adsorbent for the removal of phenol from aqueous solutions. Furthermore, thermodynamic parameters including Gibbs free energy (ΔG°), enthalpy (ΔH°) and entropy (Δs°) were also determined. The results indicating the adsorption is spontaneous and endothermic process.

Keywords: Zeolite LTL, Activated carbon, Phenol, Adsorption isotherm

Introduction

Phenol is one of the crucial pollutants released from wastewater originating from various industries such as pulp and paper, tanning, textile, plastics, ferrous industries, etc. (Uddin, Islam, & Abedin, 2007). This pollutant which causes adverse effects on public health and environment. According to United States Environmental Protection Agency (USEPA), the amount of phenol concentration in surface water is limited to be no higher than 1μg/L (Girish & Murty, 2014). Moreover, phenolic compounds are very toxic at low concentrations and carcinogenic properties. They can be damaged the respiratory and gastrointestinal tracts and genetic damage (Damjanovic´ et al., 2010). The reduction of phenol concentration in industrial wastewater to clean and safe are very important. Various treatment methods such as adsorption (El-Aassar, El-Kady, Hassan, & Al-Deyab, 2016), ion exchange (Elkady et al., 2015), biodegradation, membrane separation, pervaporation, and solvent extraction have been reviewed by Girish and Murty (2012) to remove phenolic compounds from aqueous solution. Adsorption has been the most preferred technique because it takes a low cost and it is easy for a design of adsorption process. In line with this idea, Girish and Murty (2012) confirm that agricultural by-products from activated carbon production can be effective materials for phenolic compounds removal process.

Activated carbon was used as an effective adsorbent for the phenol adsorption, due to its exhibiting good texture properties, adequate surface functional groups and high adsorption ability for removal pollutants (Dabrowski, Podkościelny, Hubicki, & Barczak, 2005; Girods et al., 2009). However, activated carbon is too costly and hard to be regenerated after the adsorption process (Damjanovic´ , Rakic´, Rac, Stošic´, & Auroux, 2010; Cheng, Gao, Cui, Ma, & Li, 2016). A number of studies have been carried out as an attempt to look for cheap, effective adsorbents (Girods et al., 2009) and alternative adsorbents to remove phenols from aqueous solutions. A study by (Cheng et al., 2016) investigated the properties of zeolite X/activated carbon composite (X/AC) and found that the adsorption abilities of X/AC was more effective adsorbent for the phenol adsorption

than that zeolite X and AC. The adsorption of phenol and three chlorophenol isomers was also studied using activated carbon, NaY and Ni/NaY zeolite as adsorbents (Okolo, Park, & Keane, 2000). The result showed that time to ensure adsorption equilibrium on activated carbon was obtained within 2 - 4 h, shorter than zeolite samples. The effect of pH on the adsorption of phenols onto natural zeolite was reported by Yousef and El-Eswed (2009) Their study showed that there are 2 types of interaction that is interaction of aromatic ring of phenols with the hydrophobic sites of zeolite and the phenolate complexation with metal ions on the hydrophilic sites of zeolite surface (Yousef & El-Eswed, 2009). Moreover, adsorption by hollow structured magnetic zinc oxide nanotubes were successfully synthesized, which allows prediction the studied chemisorption process (Elkady et al., 2017).

In order to find out effective adsorbents, this study primarily focused on zeolite LTL, a one-dimensional structure of 7 Å diameter channels as an effective adsorbent. The performance of zeolite LTL in many applications depend on crystal size and morphology that supported by the previous work (Insuwan & Rangsriwatananon, 2012). Zeolite is of particular interest because of their capacity to be regenerated while keeping their initial properties. However, there is no data available in literature about removal phenol using zeolite LTL before. The objective of this work to compare the efficiency of solids adsorbent for removing phenol from aqueous solutions. The effect of pH on the adsorption of phenol were investigated. Finally, the optimum process temperature was studied.

Methods and Materials

Materials

A stock solution of phenol (1000 mg/L) were prepared and suitably diluted to the initial concentrations (5-20 ppm (mg/L)) was prepared by diluting the stock solution. The activated carbon used as adsorbent were supplied by Aldrich. The other chemicals zeolite LTL, K-LTL and H-LTL were synthesized by a method modified from Insuwan and Rangsriwatananon (2012) and Insuwan and Rangsriwatananon (2014). The aluminum hydroxide was dissolved in potassium hydroxide solution and refluxed at 120 °C until the solution became clear (solution A). Then a silica suspension was prepared (solution B). Solution A was added to solution B drop-by-drop with constant stirring for 3 minutes. The starting gel was subsequently transferred into a Teflon-lined autoclave for crystallization at 453 K for 2 days without stirring. Then, the Teflon-lined autoclave was cooled in cold water before opening. Finally, the product was washed several time with DI-water until the pH of supernatant became neutral and dried for overnight at 373 K in an air oven. H-LTL was prepared by ion-exchanging K-LTL with 1 M NH_4NO_3 solution and subsequently calcined at 723 K for 4 h.

Batch experiments

The batch studies were done by shaking 0.01xx g of the solid adsorbent in 100 mL of the initial concentrations of phenol (5-20 ppm (mg/L)) at 303, 313 and 323 K, respectively, for 24 h to ensure that equilibrium was attained. Next, the adsorbent was separated by centrifugation at 5000 rpm for 5 min. Finally, the residual of phenol concentration in supernatant was analyzed using UV-vis spectroscopy at 510 nm by the 4-aminoantipyrine method (Cheng et al., 2016). The phenol adsorption capacity qe (mg/g) for each concentration of phenol at equilibrium was calculated as follows equation 1.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 (mg/L) and C_e (mg/L) are initial and equilibrium concentrations of phenol in solution, respectively; m (g) is the weight of solid adsorbents; and V (L) is the volume of the liquid phase.

Results and Discussion

Adsorbent characterization

The structures of zeolites before and after adsorption of phenol was confirmed by X-ray powder diffraction patterns (Model D5005, Broker, CuKα radiations). The results revealed that zeolites preserved their structures unaffected after the adsorption and regeneration process (figure not investigated). The specific surface area and micropore surface area of adsorbent were determined from nitrogen adsorption isotherms obtained at -196 °C provided by Aotosorb 1-Quantachrome Instrument, USA.

Effects of the adsorbent and adsorption isotherm

The adsorption of phenol on solid adsorbent can be explained by the Langmuir and Freundlich isotherm models. The Langmuir isotherm equation is based on (i) the surface of adsorbent is in contact with an adsorbate which is strongly attracted to the surface (ii) the adsorption takes place at specific homogenous sites on the surface of the adsorbent (iii) the adsorption involved the attachment of only one layer of molecules to the surface. (Cheng et al., 2016; Insuwan & Rangsriwatananon, 2014):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the Langmuir constant related to energy of adsorption.

Freundlich isotherm equation is based on the adsorption on a heterogeneous surface and possibility of adsorption on multilayer.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (3)$$

where K_F (mg/g)(L/mg)$^{1/n}$ and n are Freundlich adsorption constants which correspond to adsorption capacity and adsorption intensity, respectively (Insuwan & Rangsriwatananon, 2014).

Table 1 Parameters of the models of Langmuir isotherm for the phenol on solid adsorbent

Adsorbent	Temperature (K)	Langmuir isotherm parameters		
		q_m (mg/g)	K_L (L/mg)	R^2
K-LTL	303	196	0.18	0.9473
	313	200	0.41	0.9666
	323	208	0.59	0.9752
H-LTL	303	158	0.20	0.9639
	313	144	0.33	0.9858
	323	182	0.69	0.9938
AC	303	138	0.24	0.9746
	313	147	0.26	0.9604
	323	161	0.62	0.9981

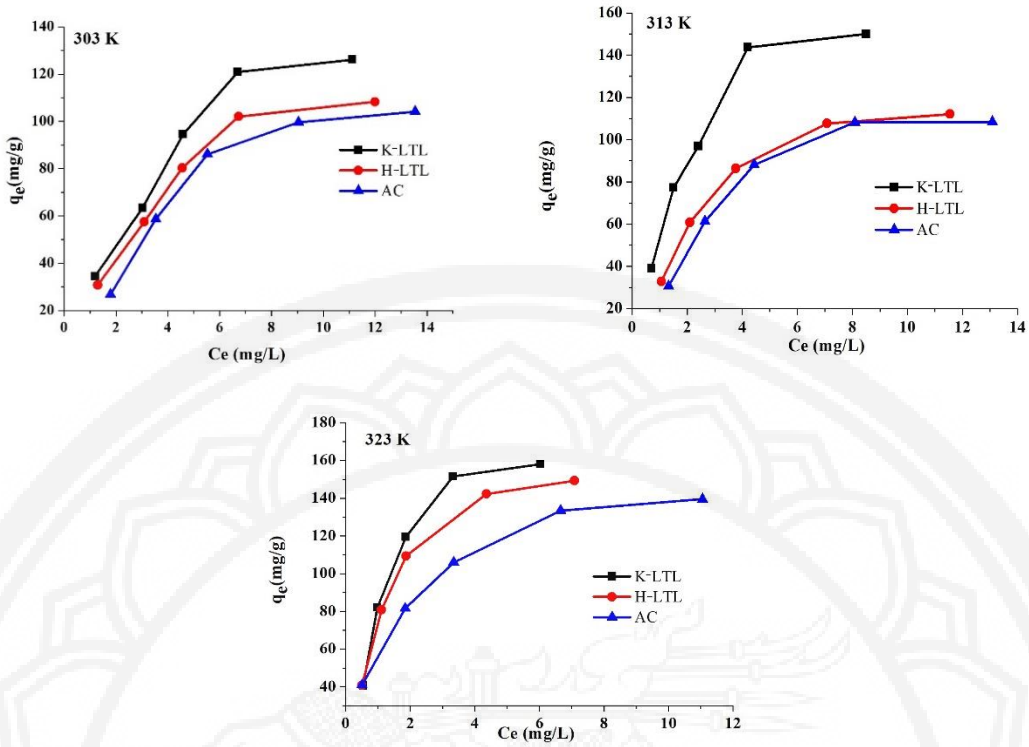

Figure 1 The adsorption isotherms of phenol from aqueous solution onto K-LTL, H-LTL and AC at 303, 313 and 323 K

The efficiency of adsorbents played important role for industrial applications that is related to the pore structure and the surface characteristics of the adsorbents (Nevskaia, Santianes, Muñoz, & Guerrero-Ruíz, 1999). The adsorption isotherm and Langmuir isotherm of phenol adsorption on activated carbon (AC), H-LTL and K-LTL zeolite are shown in Figure 1 and 2. As shown in Table 1, the phenol adsorption capacity on AC (138-161 (mg/g) is lower than that of H-LTL (158-182 (mg/g)) and K-LTL (196-208 (mg/g)). The adsorption capacity is increase for higher surface area and volume of zeolite LTL (See Table 2) (Insuwan & Rangsriwatananon, 2014). Thus, the increased accessibility of active site of zeolite LTL also leads to improve the adsorption capacity. In addition, molecule dimension of phenol is 0.57 nm in length and 0.43 nm in thickness (Lorenc-Grabowska, 2016), which are smaller than that of the free diameter of 0.71 nm of zeolite LTL pores. Thus, phenol was able to access the zeolite LTL.

Table 2 Pore structure parameters of the adsorbent

adsorbent	Surface area (m^2/g)	Micropore surface area (m^2/g)
K-LTL	348	322
H-LTL	390	353
AC	151	141

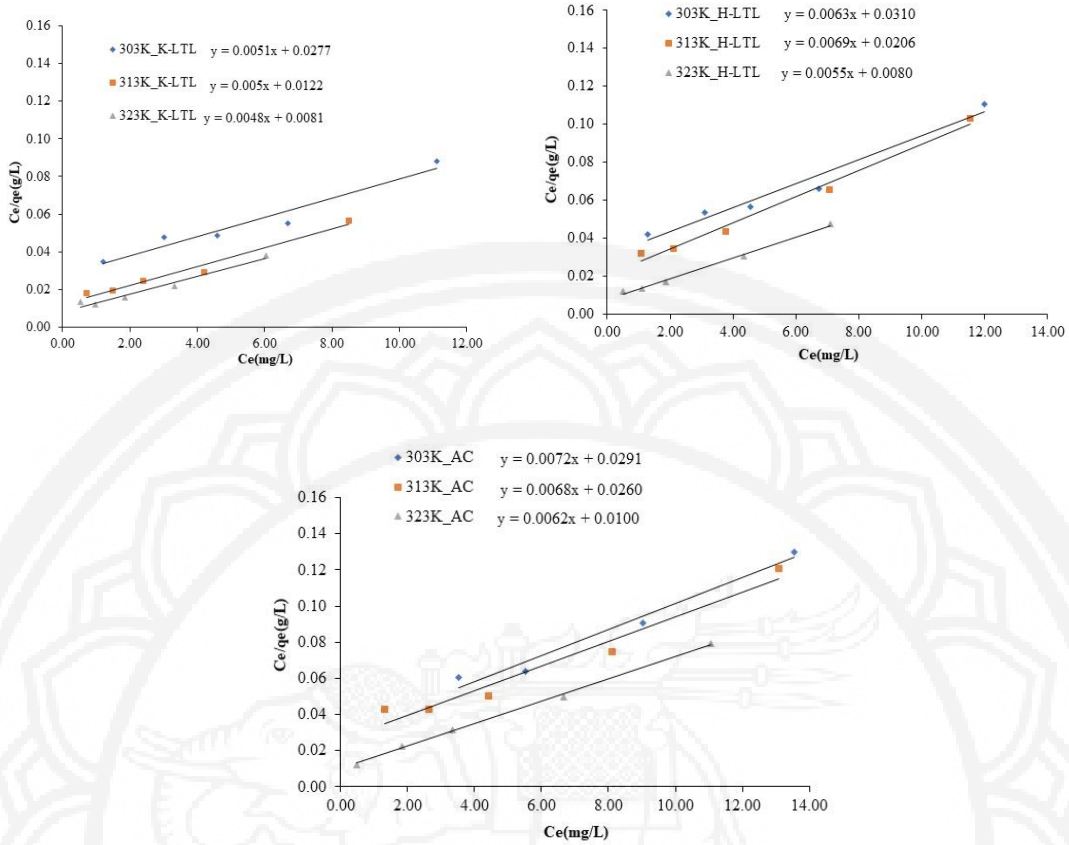

Figure 2 Langmuir isotherm of phenol on various solid adsorbent at 303, 313 and 323 K

The interaction of the phenol molecule with adsorbent are also considered. Firstly, hydrogen bonding between hydrogen atom of phenol and framework of H-LTL zeolite. Second, cation- π interaction between π electron of aromatic ring of phenol with K^+ ion of K-LTL can occur. The interaction of phenol on AC involved the formation of electron donor-acceptor complexes (Okolo et al., 2000; Nevskaia et al., 1999). Finally, it can be confirmed that K-LTL zeolite is a good adsorbent for removal of phenol due to its large pore structure and favorable interaction characteristics of its framework.

Effects of the solution pH

Phenol is a very weak acid and can lose a hydrogen ion and forms phenolate ion at the pH above the pka (9.89). The phenol adsorption on K-LTL zeolite was investigated at pH range of 2-10 was illustrated in Fig.3. The results showed that the adsorption is increase at pH of 4 and decrease with increasing pH of the solutions. At pH of 4, it has been shown that hydrogen bonding hydrogen bonding between hydrogen atom of phenol and framework of zeolite LTL (Nevskaia et al., 1999; Tan, Ahmad, & Hameed, 2008. The phenol removal has gradually increased at pH of 10. It is proposed that at the pH above the phenol pka (9.89) (Cheng et al., 2016) the phenol is presented as phenolate ions ($C_6H_5O^-$). Complexation of phenolated anion with extraframework cation (K^+) on the zeolite can be occurred (El-Naas, Al-Zuhair, & Alhaija, 2010; Arana & Mazzoco, 2010). Hence in the study, the pH of 4 was suitable as the optimum pH value on phenol adsorption.

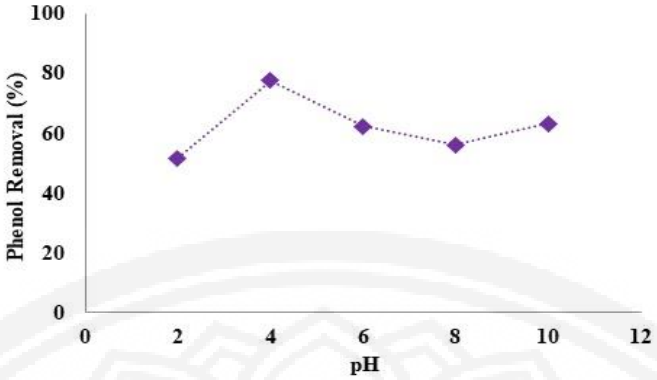

Figure 3 Effect of pH on the adsorption of phenol on K-LTL, initial concentration = 15 mg/L, temp = 303 K)

Effects of the temperature

Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process. The phenol removal was increased with increasing temperature then the adsorption is an endothermic process (Insuwan & Rangsriwatananon, 2014). This may be the enlargement of pore size and activation of the adsorbent surface with temperature. With increasing temperature, probably increased mobility of phenol to penetrate into pore of zeolite LTL (Tan et al., 2008).

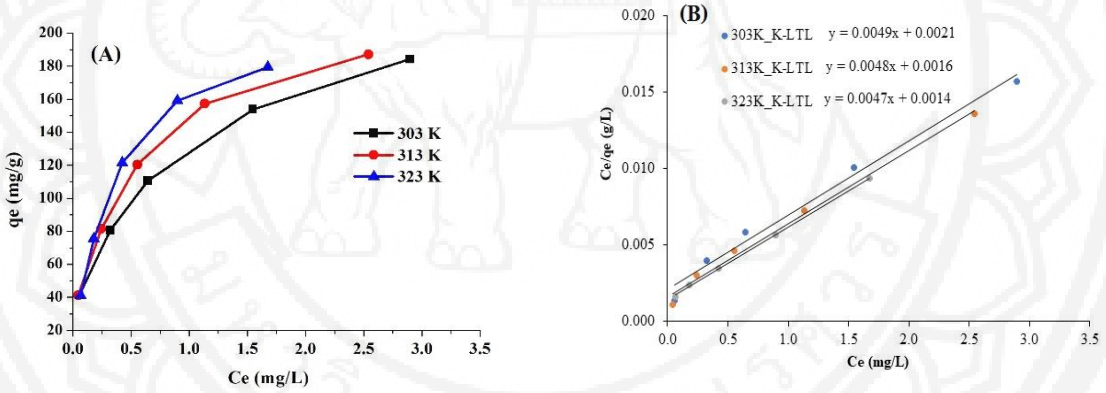

Figure 4 Adsorption isotherms (A) and Langmuir isotherm (B) of phenol on K-LTL at 303, 313 and 323 K

Figure 4. show adsorption isotherms and Langmuir isotherm of phenol on K-LTL. The equilibrium data were fitted to the Langmuir equation that predicted the monolayer coverage of phenol onto K-LTL. From table 3 it was also observed that the maximum sorption capacity of K-LTL for phenol was found to be 204 - 213 mg/g. The comparison of maximum adsorption capacity (q_m) of phenol onto various adsorbents is presented in Table 3. From above mention, to our knowledge, direct information on phenol removal from aqueous solutions can be applied K-LTL zeolite as an adsorbent to treating wastewater in industry.

Table 3 Comparison of monolayer adsorption capacity for phenol onto other various adsorbents.

Adsorbent	q_m (mg/g)	Reference
Date pit	262.30	(El-Naas et al., 2010)
Black stone cherries	133.33	Rodríguez Arana and Mazzoco (2010)
Beta zeolite (Si/Al =43)	67.76	Damjanovic´ et al. (2010)
Luffa cylindrical fiber	9.250694	Abdelwahab and Amin (2013)
Lantana camara (HCl treated)	112.5	Girish and Murty (2014)
Lantana camara (KOH treated)	91.07	
Zeolite X/activated carbon composite (X/AC)	37.92-40.79	Cheng et al. (2016)
ZnO nanotubes	20.41	Elkady et al. (2017)
K-LTL	204-213	Present work

Thermodynamic parameter

Standard Gibbs free energy (ΔG°) can be calculated from the following equation 4 (Insuwan & Rangsriwatananon, 2014).

$$\Delta G^\circ = -RT\ln KL \quad (4)$$

where R is the gas constant (kJ/mol K), T is temperature (K), and K_L is Langmuir constant. Moreover, entralpy change (ΔH°) and entropy change (ΔS°) were calculated using the following equation 5.

$$\ln K_L = -\frac{\Delta H^\circ}{TR} + \frac{\Delta S^\circ}{R} \quad (5)$$

Table 4 Thermodynamic parameters for phenol adsorption on K-LTL under different temperatures.

Adsorbent	Temperature (K)	ΔG° (KJ/mol)	ΔH° (KJ/mol)	ΔS° (KJ/mol/K)
K-LTL	303	-2.13	14.86	3.66
	313	-2.86		3.78
	323	-3.25		3.90

The results of thermodynamic parameters are shown in Table 4. The negative values of ΔG° (-2.13 to -3.25 kJ/mol) indicates spontaneous nature of the adsorption process. The positive values of ΔH° (14.86 kJ/mol) indicates that the adsorption of phenol onto zeolite LTL is an endothermic reaction and a physical adsorption process that agrees with the several reports (Bhattacharyya & Sen Gupta, 2006; Fungaro, Yamaura, & Carvalho, 2011). Moreover, the positive value of ΔS° indicates an increased in randomness at the solid-solution interface during the adsorption process.

Conclusion

The present study confirmed that the K-LTL zeolite was found to be suitable adsorbent for the removal of phenol. Equilibrium data was fitted in a Langmuir isotherm equation. The adsorption capacity of K-LTL zeolite was found to be 204-213 mg/L at pH 4. The high adsorption capacity of phenol on zeolite K-LTL was explained in terms of the stronger interaction (cation- π interaction between aromatic ring of phenol with extraframework cation, K^+). In addition, the thermodynamic parameters confirm that the spontaneous and endothermic nature of adsorption process. The above results suggest that the zeolite in potassium form (K-LTL) could be used as an effective adsorbent for the removal of phenol from aqueous solutions.

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