Removal of Phenol by Zeolite

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Received: *5 April 2016*
Revised: *20 April 2016*
Accepted: *12 May 2016*
In press: *13 May 2016*
Online: *30 June 2016*

Keywords:
Phenol; zeolite; adsorption; adsorbent

Abstract

The adsorption of phenol by Zeolite was investigated to assess its possible use as an adsorbent. The adsorbent properties were tested on batch solutions containing minimum concentration of 3mM (282 ppm) and a maximum of 7mM (658ppm) phenol, at fixed temperature of 30°C without pH adjustment. The effect of the adsorbent dose, contact time and initial phenol concentration on the removal degree of phenol was investigated. Effect of the adsorbent dosages for the removal of phenol was carried out using adsorbent dosages ranging from 5g to 25g. After hours of adsorption, this experiment reveals that the phenol removal performance is varied based on the three parameters investigated. For IPC 3mM, 5mM and 7mM; 25g, 15g, 5g is considered as the optimum dosage with phenol removal of 49%, 67% and 68% respectively. The equilibrium sorption data was better explained by Langmuir isotherm model suggesting that the adsorption of phenol observed monolayer sorption pattern.

Introduction

Phenol is harmful to organisms even at low concentrations. Industries as refineries, coking operations, coal processing, plastics, wood products, as well as pesticide, paint and paper industries produces wastes containing phenol. Removing phenol from water is very crucial, therefore to date, many methods; physical, physico-chemical, chemical, and biological methods have been reported (Lin *et al.*, 2009; Singh *et al.*, 2012). Adsorption is well-established and powerful technique for treating wastewater from industry and domestics. Because of its very effective, low-cost and widely used for the removal of the phenolic pollutants, adsorption generally considered the best method (Ihsan, 2013). Activated carbon is the most commonly used adsorbent. However, difficulties and high cost in carbon regeneration makes economic, stable and efficient adsorbents desirable. Zeolites are an important class of aluminosilicates used as catalysts and adsorbents (Guisnet and Gilson, 2002). These adsorbents are stable, renewable, and present a high absorption capacity (Khalid *et al.*, 2004; Kuleyin, 2007; Koubaissy *et al.*, 2011). Previously, Roostei and Tezel (2004) have conducted an experiment to examine the liquid-phase adsorption of phenol from water by silica gel, HiSiv 3000(Zeolite ZSM-5 structure), activated alumina, activated carbon, Filtrasorb-400, and HiSiv 1000(Zeolite-Y structure). Results of kinetic experiments indicated that HiSiv 1000 had the highest rate of adsorption among the adsorbents studied. Similarly, Bizerea *et al.* (2013) investigated zeolite–cellulose composite called BioZheolith and suggested to consider this material able to be employed for the removal of phenol from wastewater. In this respect, the present study explores the adsorptive removal of phenol by Zeolite (clinoptilolite) by investigating the effect of IPC, adsorbent dose and contact time.

Methodology

Reagent

Reagent grade phenol (99.9%) from Sigma-Aldrich Chemie GmbH, Germany was used to prepare phenol solutions. The phenol concentrations in the initial samples and in those subjected to adsorption were analyzed by isocratic elution high performance liquid chromatography (HPLC Agilent) (W600 2487) using a Waters Hypersil C18 5µm (4.6mmx250 mm) column with UV detector at 280 nm. A Ramsay media as described by Ramsay (1989) containing (g/L): 2.0g NH_4NO_3 , 0.5g KH_2PO_4 , 1.0g K_2HPO_4, 0.5g $MgSO_4$ $.7H_2O$, 0.01g CaCl $.2H_20$, 0.1g KCl and 0.06g yeast extract is added to the phenol solution for optimization purpose for further experiment (not shown here).

Preparation of Zeolite

Natural zeolite (clinoptilolite) samples were used in this study supplied from Slovakia. Prior to the experiment, the zeolite was passed through a No. 10 sieve, then it was washed (using magnetic stirrer, Thermo Scientific Cimarec) twice with 4L distilled water (each for 4h) to remove the impurities and dried in an oven at 70±5°C overnight in an oven (115 V RE 53 Binder). The dry samples were stored in airtight glass containers without further treatment for prior analysis.

Adsorption Experiment

An adsorption isotherm describes the relationship between the amount of adsorbate that is adsorbed on the adsorbent and the concentration of dissolved adsorbate in the liquid at equilibrium. Accurately weighed portions of adsorbent were placed into a series of 250-ml conical flasks. Different amount of adsorbent was used for different bottles to determine the isotherm. After the addition of 200 ml of phenol solution (with Ramsey media), conical flasks were sealed with aluminum foil. Initial concentration of phenol in liquid phase was same for the entire flask. The bottles were placed in an incubator at 30±5°C until they reached equilibrium. The flasks were then taken off the incubator and the suspensions were left standing for a while to allow the adsorbent particles to settle. 1 milliliter of the sample was collected periodically, filtered through filter syringe to remove any remaining adsorbent particles and was taken for HPLC analysis.

Result and discussion

Effect of adsorbent dosage

It can be observed from Figure 1, that bigger dose of adsorbent gives higher number of adsorption sites (Lin et *al.*, 2009). The rise of the adsorbent dosage from 5 to 25 g determines a growing efficiency of phenol removal from 32 to 49% in the 3mM phenol solutions. However, a greater dose of Zeolite, up to 25 g, produces a much smaller rise of the phenol removal, leading to a plateau in 5mM and 7mM solution. It can be determined that optimum dosage contribute to higher phenol removal is 15g of adsorbent dosage for IPC 5mM, as further increases in the dose of adsorbent results in the removal remaining almost constant, which could be attributed to saturation of the binding sites (Mohan, 2009). The adsorption capacity is high at low doses and low at high doses of adsorbent for IPC of 7mM. 68% of phenol is removed by 5g adsorbent. Increasing the adsorbent dose up to 25g shows no positive influence in phenol removal. Similar with other published data (Han *et al.*, 2006; Lin *et al.*, 2009), the adsorption capacity is decreasing while the adsorbent amount increases. This fact seems apparent if we consider the definition and calculation of the adsorption capacity. The adsorbed quantity per adsorbent unit of mass remains constant as the number of active sites remains constant, along with the rise of the adsorbent mass. However, the number of units of mass grows faster than the quantity adsorbed onto them, thus resulting into a reduction of the adsorption capacity value.

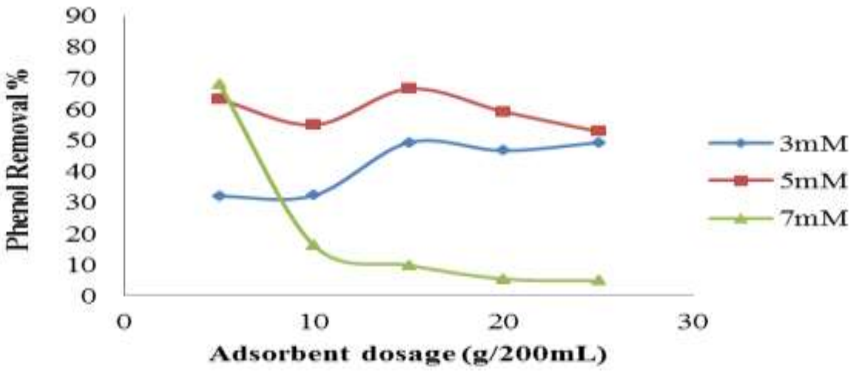

Figure 1: Effect of adsorbent dose on the removal percentage of phenol adsorbed on zeolite

Effect of contact time

By increasing the contact time, the phenol removal percentage increases for adsorbent dosage of 20 and 25g in 3mM IPC as shown in Figure 2. In the presence of a low concentration of phenol in the solutions, the rise of adsorbent will prepare a lot of easily accessible sites which will remove more phenol (Bizerea *et al.*, 2013). The rate of phenol removal was found to be rapid during the initial 60 minutes for all dose of adsorbent, which can be attributed to the availability of sites. The phenol removal rate is remained nearly constant thereafter for dose of adsorbent 5, 10 and 15g.

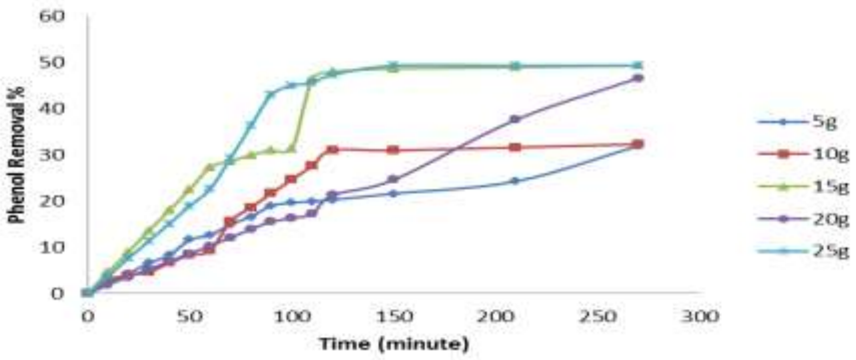

Figure 2: Effect of contact time on the removal of phenol at IPC 3mM

Figure 3 illustrates that the phenol removal was fast for IPC of 5mM with adsorbent dose of 10g, which remove phenol by 55% by the first 80 minutes. When the adsorbent dose is 5g and 15g, the phenol removal of 63% and 52% was achieved after 120 and 110 minutes of contact times respectively. The phenol removal is nearly constant for adsorbent dose of 15 and 20g after 150 minutes. This may be due to the fact that after some initial period, slower adsorption may be attributed to the slower diffusion of phenol into the interior pores of zeolite (Motsi *et al.*, 2009).

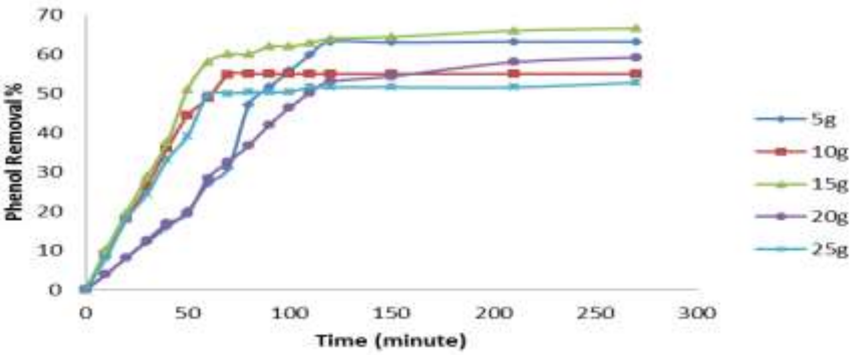

Figure 3: Effect of contact time on the removal of phenol at IPC 5mM

Figure 4 is the effect of contact time for IPC 7mM. The phenol removal rate only increase with longer contacts time in adsorbent dose of 5g, by 68%. When adsorbent dose of 10, 15, 20 and 25g is applied, very low of phenol is removed. This is similar with published data (Bizere *et al.*, 2013), at higher concentrations, phenol adsorption presents a saturation trend as the adsorbent offers a limited number of surface binding sites.

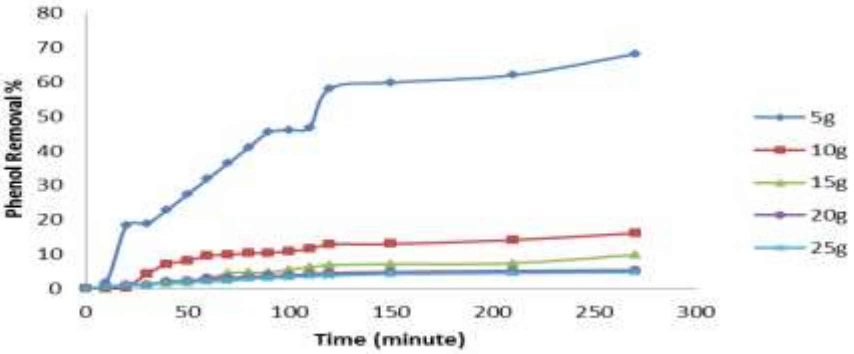

Figure 4: Effect of contact time on the removal of phenol at IPC 7mM

The first indicator for an adsorbent to be suitable for phenol removal from wastewater is they reach the equilibrium constitute with a fast adsorption in a short period of time. Some cases reached the plateau shows that the adsorbent surface is saturated from the point onward. This can be described that, over time, the number of actives sites reduces and the adsorbent becomes more crowded, impeding the free movement of the adsorbent within the adsorbent particles (Kennedy *et al.*, 2007).

Effect of initial phenol concentration

The initial phenol concentration was varied from 3mM to 7mM. It can be noticed in previous Figure 2, 3 and 4, taking 5g of adsorbent dose as a reference, the phenol removal varies from 32% to 68% when phenol concentration rises from 3mM to 7mM. The adsorption of phenol by zeolite increase as the initial phenol concentration increased.

Increasing the initial phenol concentration would result in higher phenol adsorption as the mass transfer driving force will be higher. High concentration of phenol contributes a higher interaction between phenol and adsorbent. Thus, a higher initial phenol concentration enhances the adsorption process. On the other hand, the adsorption yield drops as the phenol initial concentration elevates. Phenol presents in the adsorption medium could interact with the binding sites at lower concentration, so higher adsorption yields have been obtained while the adsorption sites saturated at high concentration, resulted in lower adsorption yields (Dursun and Kalayci, 2005; Dursun *et al.*, 2005). However, in this experiment the adsorbent dose influence the effect of initial phenol concentration.

Adsorption isotherm

Sorption isotherms are used to describe the interaction between phenol and the adsorbent. Equilibrium studies were performed by adding an accurately weighed 15 g of natural zeolite to 250 ml conical flask containing different initial phenol concentrations of 3, 5 and 7mM. The suspensions were placed in an incubator at 30°C allowed to equilibrate for 280 min. The phenol adsorptions were analyzed according to the Langmuir and Freundlich models in order to describe the relationship between the amount of phenol adsorbed and its equilibrium concentration in solution. The experimental data obtained for phenol adsorption on Zeolite has been used to plot the linearized form of each isotherm model. The isotherm constants and correlation coefficients of the adsorption models are presented in Table 2.

Table 2: Isotherm parameters by Langmuir and Freundlich models

Models	Constants					
	R^2	q_{max} (mg/g)	R_L	k_L (L/g)	k_F (mg/g)	1/n
Langmuir isotherm	0.993	0.707	0.278	0.092	-	-
Freundlich isotherm	0.681	-	-	-	13.0	0.835

As shown in Table 2, it is clear the Langmuir model exhibited a better fit to our adsorption data than the Freundlich model suggesting that the monolayer coverage of the adsorbate at the outer surface of the adsorbent is significant. According to Langmuir isotherm equation, the maximum adsorption capacity, qmax, of phenol on Zeolite has reached the 0.707 mg g^{-1} value. The R_L value is 0.278, in the range of 0 to 1, proving that phenol adsorption is favorable on Zeolite. The correlation coefficient of Freundlich model is lower compared to Langmuir isotherm model. The value of 1/n for phenol adsorptions onto Zeolite, is between 0 and 1 attesting that chemisorption takes place. The fact that this parameter is not very close to 0 indicates that the adsorbent surface is less heterogeneous.

Conclusion

The phenol adsorption by zeolite clearly depends on some parameters such as contact time, adsorbent dose and initial phenol concentration. The Langmuir isotherm was found to adequately describe the uptake equilibrium, confirming the monolayer adsorption capacity. In low initial phenol concentration, phenol can be removed more in shorter period of time with higher adsorbent dose. However, in higher initial phenol concentration, less adsorbent dose and longer contact time is required to remove more phenol. Multi stage adsorption may be employed to remove more phenol with higher initial phenol concentration, even though the cost of operation needs to be considered. This idea will be tackled in further investigations.

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