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Preparation of an Adsorbent from Pumice Stone and Its Adsorption Potential for Removal of Toxic Recalcitrant Contaminants

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ABSTRACT

Background: In recent years, proficient treatment of wastewaters containing recalcitrant and toxic compounds such as phenol has been a challenge. This study introduced and evaluated an efficient option for treating such wastewater.

Methods: This experimental study was performed on phenol removal as a recalcitrant and toxic compound in aqueous solutions in 2011. The pumice stone was collected from a local mine. Collected samples were crushed and granulated using standard sieves (mesh size of 20). CuSO₄ was used to modify prepared samples. The chemical composition and the surface area of the modified pumice were evaluated using X-ray fluorescence and N₂ gas via Brunauer-Emmett-Teller isotherm and Belsorb software. Different parameters including of pH (3-12), contact time (20-120 min), phenol concentration (25-400 mg/L) and adsorbent dosage (0.25-1 g/L) were examined in a batch reactor.

Results: 93.5% of the phenol was removed under optimum experimental conditions of pH 3 and a 0.5 g/L adsorbent dose after 60 min contact time. The experimental adsorption isotherm the best fit with Freundlich equation model. The maximum amount of phenol adsorption onto modified pumice (MP) was 15.8 mg/g.

Conclusion: Modified pumice is effective adsorbent for the removal of phenol from aqueous solution. Accordingly, it is feasible and promise adsorbent for treating polluted phenol streams.

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Introduction

Phenol compounds as toxic, resistant to microbial attack are extensively used in industries and have become common pollutants in water bodies. Due to their stability and bioaccumulation, they remain in the environment for longer periods. Therefore use of an effective and economic method for the elimination of phenol in water solutions has been in critical demand¹⁻⁵. Traditional treatment methods presented in scientific literatures for removing phenol are classified into three major categories including physical, biological, and chemical methods like adsorption, advanced oxidation, wet and chemical oxidation, and biological processes^{5, 6}. Among these methods, adsorption process is one of the promising alternative methods used for the removal of recalcitrant compounds from water and wastewater. Activated carbon is the most extensively used adsorbent. However, the production of activated carbon is expensive, making this method economically non-efficient^{7,8}. Hence, the most

important challenge for applying the adsorption method to recalcitrant compounds adsorption is resulting a low-cost adsorbent which are used easily and are cost-effective. Therefore, adsorption process can be successfully competed with other recalcitrant compounds removal methods. In this regards, studies have been devoted to low-cost materials such as local mineral for the removal of recalcitrant pollutants from water and wastewater⁹⁻¹¹. One such local mineral is pumice.

Pumice is a light, highly porous (pore volumes up to 85%) volcanic stone. Due to its microporous structure it has a relatively high specific surface area. Pumice stone can exhibit acidic or basic character. Pumice stone has a high silica content (generally 60–75% SiO₂), which makes it abrasive. The high porosity of volcanic pumice rock and its richness in silica, alumina makes this material a promising candidate as an adsorbent^{12, 13}. In addition,

others researchers have indicated that pumice is an ideal support for impregnated metal on surface it. Therefore, it is very interesting to study the capability of pumice to removal recalcitrant pollutants from wastewater.

The main purpose of the present work was to investigate the capability of modified pumice to eliminate phenol, from liquid media under different experimental conditions. The effects of main operational parameters, i.e., solution pH, mass of adsorbent, target pollutant concentration and mixing time were evaluated for phenol removal

Methods

This experimental study was performed in 2011. Modified pumice (MP) was prepared and characterized according to the procedure described previously¹³. Characteristics of modified pumice are described in our previous study¹⁴. In summary, pumices is not uniformly porous and the size of pores are less than 15.297 nm, pH of zero point of charge (pH_{zpc}) = 7.16 microspores sorbent with Brunauer-Emmett-Teller (BET) specific surface area 13.77 m²/g as determined by N₂ gas adsorption-desorption. The porosity of pumice was determined through the conventional adsorption of nitrogen at 77 K and 91.43 KP pressure⁹. Analysis of data for calculation of BET surface area and porosity was carried out by Bel-sorb software (Ver.5) (data not shown). X-ray fluorescence (XRF) data indicated that the main part of pumice structure consisted of quartz with chemical formula of SiO₂ and its other components were Al₂O₃, CaO, MgO, Fe₂O₃, Na₂O, and K₂O. For convenient evaluation of the effective parameters, the adsorption of phenol within modified pumice was performed with batch procedure. These tests were performed in a 100 ml high-density polyethylene bottles. The bottles were stirred with a shaker (Pars Azma Co) at 120 rpm at room temperature.

All chemical reagents in this study were obtained from Merck (Germany). The solutions were prepared by dissolving the adequate quantities of the compounds in distilled water. Stock solution (1000 mg/l) of phenol was prepared by dissolving of 1 gr phenol into distilled water. Experimental solutions of the desired concentrations of phenol were obtained by successive dilutions (25 to 400 mg/L) and pumice doses 0.25 to 1.00 g/100 ml respectively. For the kinetic experiments, reaction times selected to quantify phenol removal were 20 to 140 min. pH values investigated were 3, 7 and 12, respectively. Solution pH values were adjusted using reagent grade NaOH and/or HCl solutions with different molar concentrations. The pH of solutions was measured using a pH meter (Wagteck Mi 151).

For each experimental matrix, the solutions containing phenol in reactor were kept well-mixed (150 rpm) in a temperature-controlled orbital shaker and incubator (GFL 3017). After the pre-selected reaction time, the solutions were filtered through 0.45 µm membrane filter and ana-

lyzed for phenol by UV/VIS spectrophotometer (Shimadzo-1700, Japan)¹⁷ in 500 nm.

All of adsorption experiments were conducted at 25±0.5 °C and the average of the duplicated experimental results reported. The phenol removal efficiency (RE) and equilibrium adsorption capacity were calculated from Eqs. (1) and (2):

$$RE = \left(\frac{C_{ini} - C_t}{C_{ini}} \right) \times 100 \quad (1)$$

$$q_e = \frac{V}{M} \times (C_{ini} - C_t) \quad (2)$$

where C_{ini} and C_t are the initial and concentration at time t of phenol (mg/l); q_e is equilibrium phenol concentration on adsorbent (mg/g), V is the volume of solution (L), M is the mass of modified pumice used (g)¹⁵.

To evaluate the isotherm of phenol adsorption onto MP, two of the most used isotherm models (Freundlich and Langmuir) were fitted to experimental results. The linear forms of the selected models are expressed by Eqs. (3) and (4):

$$\log(q_e) = \log k_f + \frac{1}{n} \log(C_e) \quad (3)$$

Where q_e is the amount of adsorbate (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L), K_f and 1/n are the Freundlich constants. The value of K_f and n can be obtained from the slope and intercept of log q_e versus log C_e, respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} C_e \quad (4)$$

The value of b and q_m can be obtained from the slope and intercept of a plot of C_e versus C_e/q_e¹⁶.

Results

The duplicated experimental results in the terms of phenol removal and adsorption capacity as a function of contact time at versus the pH indicate in Figure 1. Phenol adsorption onto MP considerably was affected by pH values. By increasing the pH of solution from 3 to 12, the average degree of phenol removal decreased from 93.5 to 35%. Maximum phenol adsorption occurred at pH 3 as optimum pH, therefore, the rest of the experiments were carried out at this optimum pH. In addition, data in Figure 1, shows the removal efficiency increased as the contact time increased phenol adsorption on the MP reached equilibrium after 60 minutes, and then remained constant.

The effect of MP on phenol adsorption was investigated by varying the MP dose from 0.25 to 1 g/L using 100 mg/L phenol solution at pH 3.0. The results on the effect of adsorbent dose on phenol removal showed that the phenol removal efficiency increased from 60% to 93.5% as the adsorbent mass increased from 0.25 to 1 g

(Figure 2). Based on these results, the proper dose of adsorbent was determined as 0.5 g/L and was used in other parts of the study.

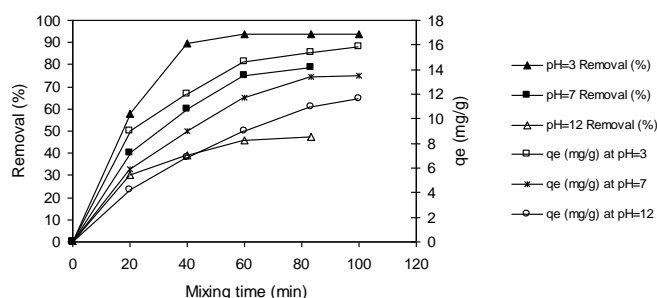


Figure 1: The effect of pH and contact time on phenol removal by modified pumice (conditions: phenol concentration= 100 mg/L, MP dose= 0.5 g/L)

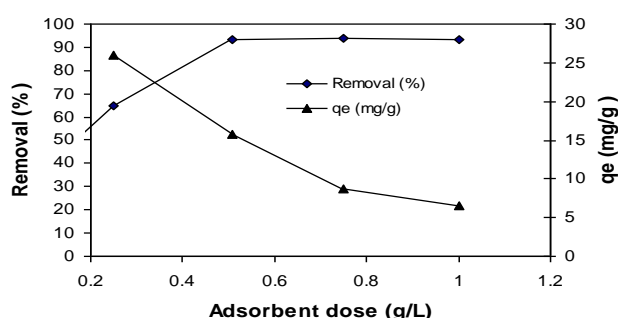


Figure 2: The effect of modified pumice dose in phenol removal (conditions: phenol concentration= 100 mg/L, mixing time 60 min, pH= 3)

The percent adsorption of 25, 50, 100, 200, 300, and 400 mg/L of phenol from aqueous solution onto MP at a pH of 3 and an adsorbent 0.5 g/L was investigated. Figure 3 shows the average phenol removal obtained from duplicate experiments and reveals an increase in percent adsorption with an increase concentration phenol from 25 to 100 mg/L. Based on data illustrated in Figure 3, the percent removal of phenol at concentrations of 25, 50 and 100 mg/L under optimal conditions were approximately 25, 65 and 93.5, respectively.

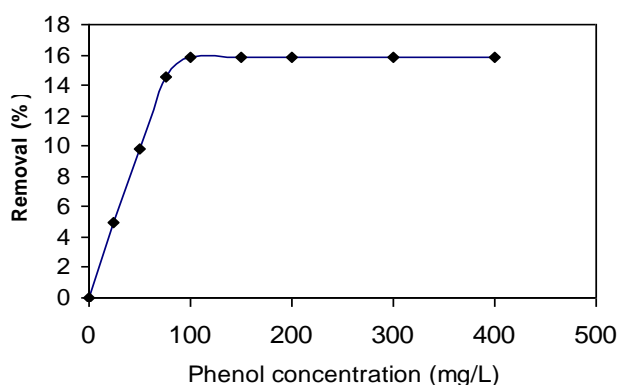


Figure 3: The effect of phenol concentration on its removal by modified pumice (mixing time 60 min, MP dose= 0.5 g, pH= 3)

Figures 4 and 5 indicate the plotted models, including the fitted models and correlation factors (R^2), and the extracted isotherm information is given in Table 1.

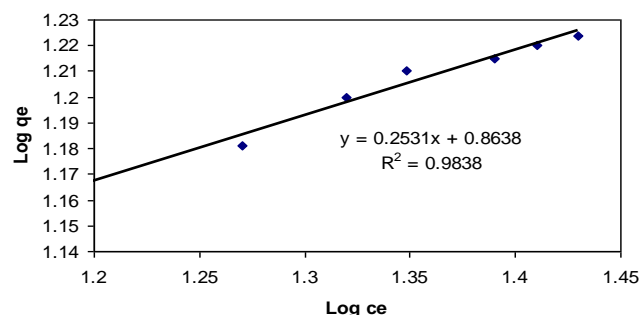


Figure 4: The linear plots of Freundlich isotherm model for phenol removal by modified pumice

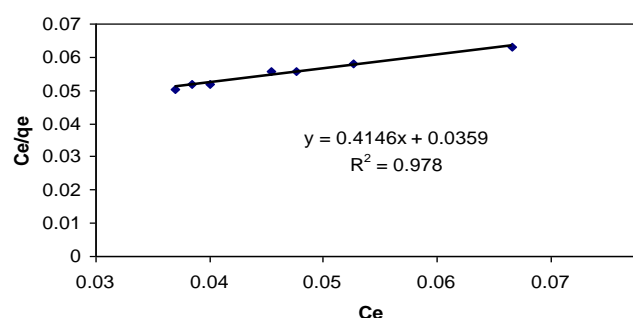


Figure 5: The linear plots of Langmuir isotherm model for phenol removal by modified pumice

The values of constants of isotherm models are consolidated in Table 1. The result indicates that both Freundlich and Langmuir models give good fit for the data. Too, the results showed that adsorption was better described by Freundlich isotherm.

Table 1: Isotherm models parameters for best-fit and corresponding correlation

Parameters	Values
Freundlich	
K_f	7.308
n	3.950
R^2	0.984
Langmuir	
b	27.850
q_m	0.086
R^2	0.978

Discussion

As Figure 1 illustrates, the highest phenol removal of 93.5% obtained at pH 3. Peak phenol adsorption at pH 3 can be explained by considering the fact that the pH of the solution influences both the surface charge of the MP as well as the molecular nature of phenol. The pK_a of phenol is 10^{-10} and the pH_{zpc} of the MP surface is 7.16, implying that phenol has anionic nature at a solution pH of 10, whereas the MP particle surfaces are negatively charged for a pH above 7.16. This means that MP particle surface was negatively charged at solution pH above 7.16 and phenol because anionic nature were repelled by MP

surface resulting in the reduction of its adsorption. However, at pH values below the pH_{ZPC} , the surface of MP particles was positively charged, accordingly, the electrostatic force of attraction between adsorbent and pollutant increases in such conditions and consequently, phenol removal efficiency increases, too. Similar data have been reported in literature^{10, 18}. These researchers have found the effect of pH on pollutant adsorption on adsorbent surface to be associated with the relationship between pH and the adsorbent surface electric charge.

It is necessary that the effects of adsorbent dose are evaluated for the optimization and selection of the best-required dose for scale-up and designing large-scale equipments¹⁹. In this regard, the results of evaluation of variation of adsorbent dose indicated (Figure 2) that the removal of phenol with increase in MP mass from 0.2 to 0.5 g/L. Attainment of a high phenol adsorption with a relatively low MP dose shows the high affinity and suitability of MP for adsorption of phenol from wastewater. The increasing adsorption efficiency with increasing MP dose can be attributed to the increase in surface area and by extension the greater number of active sites at higher adsorbent masses available for interface with phenol^{20, 21}. However, the elevation of MP dosage beyond this value was not effective significantly on phenol removal. Qadeer et al.²⁰, presented similar results. Moreover, higher doses of the adsorbent per unit volume of water resulted in the adsorbent surface overlapping and aggregation of the adsorbent molecules and consequently the total surface and the pollutant adsorption decreased²¹⁻²⁴.

In adsorption systems, the determination of the maximum adsorption capacity and development of an equation that could be accurately used for design purposes and optimization of economical equipments is important. The adsorption isotherms express the specific relationship between the concentration of sorbate and its amount adsorbed onto sorbent surface at the given experimental conditions and the equilibrium concentration of sorbate in the liquid phase. As demonstrated in Table 1, adsorption of phenol within MP comply with Freundlich with the highest values of $R^2 > 0.98$. The Freundlich model is an empirical method for adsorbents with heterogeneous adsorbing surfaces. It is known that $1/n$ in Freundlich model is the adsorption intensity and the values of $1/n$ are laying between 0 and 1 confirmed the favorable conditions for adsorption^{14, 15}. The $1/n$ of the Freundlich isotherm in this study was obtained 0.25 ($1/n = 1/3.95$). Therefore, these results suggest that surface of MP for adsorption of phenol is heterogeneous and produces a favorable adsorption condition. The results of this study differ from those of some other studies^{23, 24}. This difference may be referred to the surface properties of the given adsorbents.

Conclusion

Phenol is a very toxic and recalcitrant compound that is released into the environment throughout industrial effluents; consequently, it should be removed prior to

wastewater discharge. Adsorption processes is one of the most commonly used treatment technology for removing contaminants from water and wastewater. This study introduced a new adsorbent, MP, which is available as a mine waste material at no cost. The experimental evaluation revealed that the phenol adsorption onto MP was influenced by the pH medium and the optimum pH was 3. The removal efficiency of phenol advanced from 30 to 93.5% at 60 min contact time. The isotherm studies indicated that the Freundlich model was fitted well to adsorption data under selected condition ($R^2 > 0.98$). Optimal dosage of MP was 0.5 g/L which is lower than the dose of other adsorbent value reported in the literature for phenol adsorption by other adsorbents. Therefore MP is an efficient, cost effective and thus promising adsorbent for treating polluted phenol liquid streams.

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Conflict of interest statement

The authors declare that they have no conflict of interests.

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