Adsorptive Removal of Phenol, o- Chlorophenol and o-Cresol from Aqueous Solutions Utilizing Siliceous Rocks

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Abstract

An experimental study was conducted with Iraqi siliceous rock's powder (SRP) as a low cost adsorbent material for removal of phenol (P), o-chlorophenol (o-CP) and o-cresol (o-C) from synthetic waste water. Batch sorption tests were conducted to study isothermal adsorption capacity of the sorbent. The equilibrium sorption isotherms have been analyzed by Langmuir and Freundlich models and the various isotherm parameters were evaluated. The order of adsorbate amount adsorbed was as follows: o-CP > P > o-C. The experimental data for P and o-C were correlated well with both Langmuir and Freundlich models while those of
o-CP were correlated well with Freundlich model.

الازالة الامتزازية للفينول و اورثوكلوروفينول و اورثو كريسول من محاليلها المائية باستخدام مسحوق الصخور السيليسية

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الخلاصة

اجريت دراسة تجريبية باستخدام مسحوق الصخور السيليسيةالعراقية (كونها مادة ممتزة واطئة الكلفة) وذلك لازالة الفينول والفينول احادي الكلور و الكريسول من محاليلها المائية.اجريت اختبارات الامتزاز بطريقة الوجبة لدراسة سعة امتزاز المادة المازة في ظروف الثبات الحراري.كان ترتيب سعة المتزاز على النحو الاتي: فينول احادي الكلور › فينول › اورثو كريسول .جرى تحليل ازوثيرمات الامتزاز في ظروف الاتزان على وفق موديلات لانكميور و فريندلش وجرى تقييم عوامل الايزوثيرمات المختلفة الناتجة عن هذا التحليل.كما اشرَ التحليل نفسه الى الترابط الحسن مابين معطيات امتزاز كل من الفينول والكريسول مع موديل لانكميور بينما كان الترابط اكثر وضوحا مع موديل فريندلش في حالة الفينول احادي الكلور.

Introduction

Phenol compounds have been classified as high-priority pollutants by the USA EPA (Environmental Protection Agency, 1984).Thus, wastewaters containing phenol compounds are a serious environmental problem. Phenol compounds are usually present in wastewater generated from the paint, solvent, petrochemical, coal conversion, pharmaceutical, plastic, iron-steel and paper and pulp industries [1].

Phenols as a class of organics are similar in structure to the more common herbicide sand insecticides in that they are resistant to biodegradation,[2]. Phenols are considered as priority pollutants since they are harmful to organisms at low
concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. EPA regulation call for lowering phenol content in the wastewater below 1mg/l [3].
In the presence of chlorine in drinking water, phenols form chlorophenol, a well
pronounced medicinal taste, which is unacceptable by the World Health Organization (WHO) [4].

Several methods were used in the studies concerned with the removal of phenols from aqueous media. They include oxidation [5] , solvent extraction [6] and adsorption [7]and[8] . However, the most established and powerful method used for the treatment of domestic and industrial effluents was adsorption on solid surfaces. Several different adsorbent solids such as amberlite resin [9] ,activated carbon[10] and [11], zeolites[12] , fly ash[13] and porous clay heterostructure [14] have all been proposed to remove phenolic pollutants from wastewater. The vegetable sponge of cylindrical loofa, a natural product which grows in the north of Algeria, was used for phenol removal from wastewater [19] .
Among these, granular/powdered activated carbon as adsorbent has been widely used [15] , [16] and [17]. Activated carbon is, however, an expensive material due to the high cost and variable performance of carbon regeneration [18], so many of the other alternatives suggested become very attractive from a cost point of view.
In this work an attempt has been made to examine the utilization of siliceous rock powder as an inexpensive and efficient locally available resource for the removal of phenol and chlorophenol present in aqueous solutions.

Materials and methods

Sorbent Preparation

The siliceous rocks were obtained from the west Sahara of Iraq near Akashat town in the northwest of Al Anbar province of Iraq .The rocks were crushed into small pieces , immersed in distill water for 48 hours , then were dried at 150 ^{o} C for 24 hours .The dried rock pieces were powdered and sieved with a various mesh sieves**.** The sieved powder was thoroughly washed with double distilled water and was dried at 120ºC till constant weight. The dried powder was stored in desiccators until used. The chemical composition of Iraqi siliceous rocks was determined by x-ray. The obtained results of x-ray analysis are presented in Table 1

Table-1: Chemical composition of Iraqi siliceous rocks

Constituent	%	Constituent	%
SiO_2	**66.68**	Na_2O	**0.64**
Al_2O_3	**1.98**	K_2O	**0.14**
TiO_2	**0.09**	Fe_2O_3	**0.63**
P_2O_3	**0.96**	Others	**13.10**
CaO	**8.41**	Total	**99.07**
MgO	**6.44**		

Chemicals

Phenols solutions were prepared by diluting of stock solutions of phenols to the desired concentrations. A stock solution was obtained by dissolving 1g of each of the three phenolic adsorbate (all were ultra pure reagents obtained from Fluka Co. and were used without further purification) in 1000ml double distilled water.

Adsorption isotherms

Batch equilibrium technique was used to obtain phenols adsorption isotherms. The batch adsorption experiments were conducted by adding a fixed amount of 0.2g of adsorbent (particle size was <125 micron)to a series of 50 ml glass-stoppered flasks filled with 25 ml diluted solutions (5-300 mg/l).The pH was adjusted at 6.4for all solutions. The flasks were subsequently capped and shaken in a thermostatated water bath shaker at 25°C and agitated until equilibrium condition was attained. At the end of the equilibrium period the flasks were taken off the shaker and the samples were left standing for a while to allow the adsorbent particles to settle. 5 ml of the supernatant was removed from the flasks with syringe and centrifuged for 30 minutes at 4000 rpm. The concentrations of the clear liquid samples were then analyzed using uv-vis spectrophotometer at maximum wavelength of 270, 274.1 and 271.1 nm for phenol, o-chlorophenol and o-cresol, respectively.

The amount of adsorbate adsorbed on the adsorbent was calculated according to equation (1)

$$Qe = (C_o - Ce) / m \qquad (1)$$

Where Ce (mg/l) and Qe (mg/g) are the equilibrium adsorbate concentration in liquid and solid phase respectively, C_o (mg/l) is the initial concentrations of adsorbate and m (g) is the weight of adsorbent.

Results and Discussion

The relation, at constant temperature, between the amount adsorbed and the equilibrium concentration, is known as the adsorption isotherm.
In Figure 1, the adsorption isotherms at 25°C, of phenol, o-chlorophenol and o-cresol from aqueous solutions onto siliceous rocks powder (SRP) is presented.
It is evident that there is a marked higher adsorption for chlorophenols than that for phenol, reaching a maximum value of 27 mg/g for o-CP, 13.5 mg/g for phenol and only 11.1 mg/g for o-cresol.

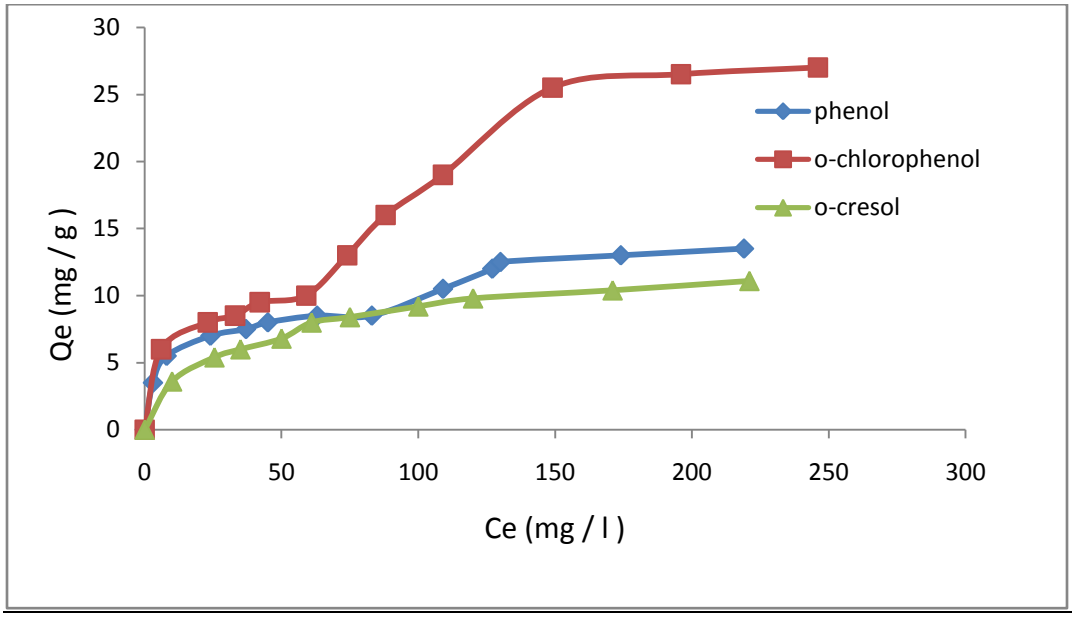

Figure 1**.** Adsorption isotherms of phenol; o-chlorophenol and o-cresol on SRP.

The study of adsorption isotherm was conducted and tested against the Freundlich and Langmuir isotherm models in order to determine the adsorption potential of SRP for the removal of phenols.
The experimental data are analyzed according to the linear form of the Langmuir isotherms. The Langmuir isotherm is represented by the following equation [20]

$$\frac{C_e}{Qe} = \frac{C_e}{Qo} + \frac{1}{bQo} \qquad (2)$$

where, Ce (mg/L) and Qe (mg/g) are the equilibrium adsorbate concentration in liquid and solid phase respectively. Qo and b is Langmuir constants related to adsorption capacity and energy of adsorption respectively. Plot of Ce/Qe vs. Ce would give the values of constants. In figure 2; the linearized Langmuir adsorption isotherms of phenol, o-chlorophenol and o-cresol are presented.

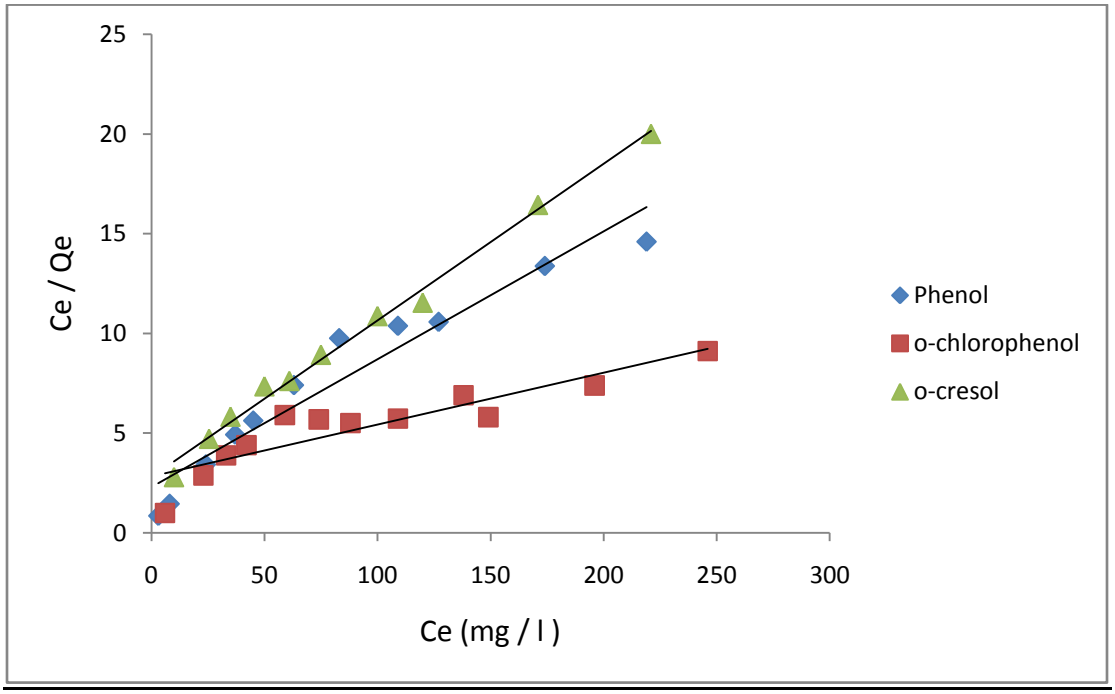

Figure 2. Linearized Langmuir adsorption isotherms of phenol; o-chlorophenol and o-cresol on SRP.

Langmuir constants are given in Table2. The nature of the adsorption process can be assessed by obtaining a dimensionless equilibrium parameter called separation factor, RL , which is used to study the applicability of Langmuir adsorption isotherm; RL is given by the relation [20]:

$$R_L = \frac{1}{(1+bCo)} \qquad (3)$$

where Co is initial concentration and b is Langmuir constant.
The magnitude of RL value reflects the nature of adsorption equilibrium: the process is non-spontaneous when RL is greater than one; favorable when RL lies between 0 and 1; and irreversible when RL is zero [22]. RL values of the systems studied were located between 0 and 1(Table 1) indicating favorable phenols adsorption on the SRP.

The Freundlich equation is expressed as

$$Qe = k\, Ce^{1/n} \qquad (4)$$

Where, k and n are the Freundlich constants and represents the measures of adsorption capacity and intensity of adsorption respectively [22]. Qe and Ce have similar meaning as in equation (2).The logarithmic form of Freundlich equation is
given in equation (5).

$$\log Qe = \log k + 1/n \log Ce \qquad (5)$$

A plot of log Ce against log Qe (figure 3) gives Freundlich constants. The values of Langmuir and Freundlich constants are presented in Table 2.

Table 2: Isotherm parameters for adsorption of phenols on SRP.

	Langmuir Constants			Separation Factor	Freundlich Constants		
Adsorbent	*Qo*	b	R^2	R_L	k	n	R^2
Phenol	15.63	0.027	0.930	0.13	2.606	3.356	0.973
o-chlorophenol	38.46	0.009	0.813	0.31	1.035	1.653	0.948
o-cresol	12.82	0.028	0.993	0.15	1.977	2.667	0.983

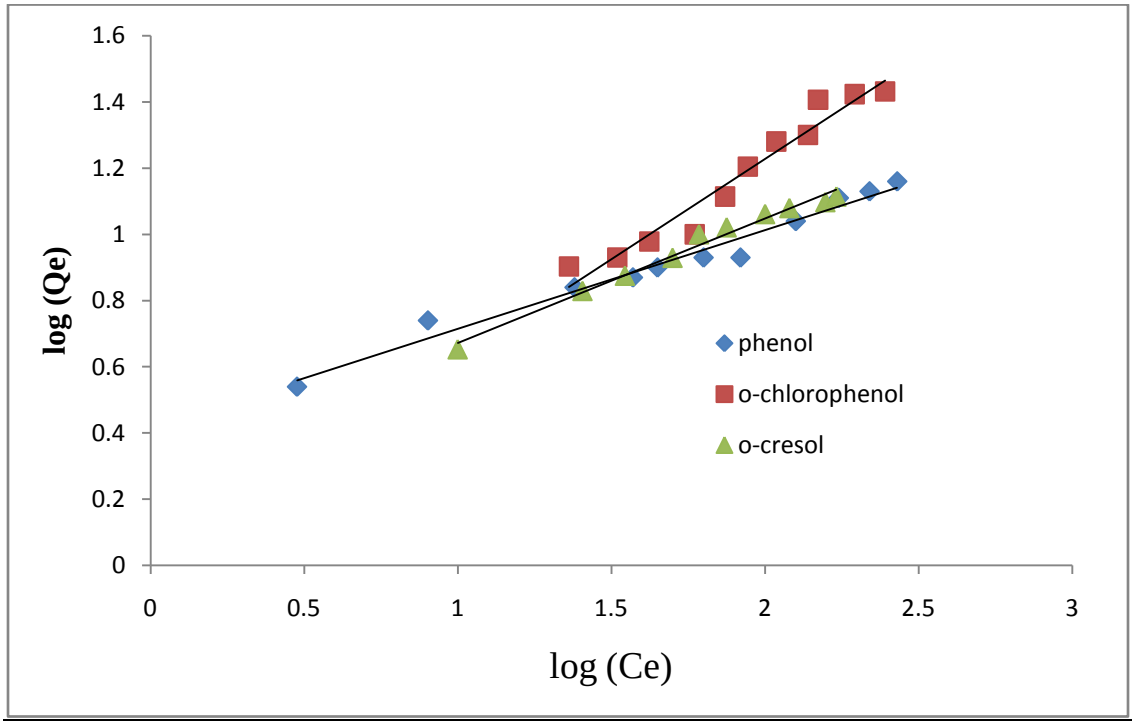

Figure 3. Linearized Freundlich adsorption isotherms of phenol; o-chlorophenol and o-cresol on SRP.

Except for o-chlorophenol case, the results that are presented in table 1 shows that the adsorption of phenols on SRP are described very well by both Langmuir and Freundlich adsorption isotherms. Such a description is indicated by the high R^2 values, being greater than 0.92 [21] .The o-chlorophenol adsorption is described better by Freundlich adsorption isotherms than by Langmuir's.

The magnitude of Qo (the Langmuir constant) indicates that the amount of adsorbate per unit weight of adsorbent (to form a complete monolayer on the surface) increasing in the order o-CP >> P > o-C.

The adsorption capacity, as indicated by the values of k (the Freunlich constant), is increasing in the order P> o-C >o-CP .However, the high magnitude of k reflects high adsorption capacity of SRP for the three phenolic compounds [23].

The adsorption parameter n in the Freundlich isotherm measures the intensity of adsorption and, hence, the preferential adsorption of one adsorbate to other [23] . Being higher than 1, the values of n indicate a strong bond between the adsorbent
and the adsorbate.

The low b (the Langmuir constant) value (< 0.3) implies low surface energy in all systems, thus indicating a probable stronger bonding between phenols and SRP [24].

Conclusions

This study has shown that local siliceous rocks can be used as effective and inexpensive adsorbent for the removal of phenol, o-chlorophenol and o-cresol from water.

Both Freundlich and Langmuir isotherms have been used to describe and illustrate adsorption process. The experimental data in the adsorption studies were fitted to Freundlich and Langmuir equations to determine the extent, capacity and degree of favorability of adsorption .The application of the constants in the evaluation and comparison of quality and capacity of adsorption was also demonstrated.

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