A study of adsorption in aqueous solution of p,o,m-Chlorophenol on Iraqi siliceouns rocks powder

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Abstract:

Adsorption of Chlorophenol compounds in aqueous solution on Iraqi siliceouns rocks powder have been investigated. UV technique has been used to determine the adsorption isotherms. The results showed that the adsorption isotherms obeyed Freundlich adsorption equation.

The adsorption was endothermic process, increasing temperature leads to increasing adsorption. ΔH, ΔS, ΔG were calculated.
The results showed that the adsorption increases with increasing acidity of solutions.

Introduction:

Chlorophenol compounds are considered as one of water polluting materials that cause tumors[1], existence of these compounds in water pose danger for water creatures[2] . Chlorophenol compounds considered as the major component for pesticide and when dissolved in water become dangerous[3] .Therefore, many researches on how to get rid of these compounds have been carried out in different methods. The adsorption on different surfaces was one of these methods[4] , surfaces like: activated carbon[5,6] ,resins[7] , Zeolite[8] were used .

In this work removal of Chlorophenol by adsorption on Iraqi siliceouns rocks powder (SRP)surface was studied.

Experimental:

1) **Material:** p-Chlorophenol (p-CP) ,o-Chlorophenol (o-CP) and m-Chlorophenol (m-CP) were supplied by BDH of 99%, 98%, 98% purity respectively, HCl supplied by BDH of 37% w/v% and deionized water had been used.
2) **Rocks**: the siliceouns rocks were supplied by (The State Company of Mining and Geological Survey).

The rocks were brought from Ukashat west of Iraq. The rocks are white color and not transparent. the chemical compositions of the rocks as it showed in Table (1) by the company.

Table (1)Result of rocks analyses

Constituent	%wt
SiO_2	66.01
Al_2O_3	2.12
Fe_2O_3	0.63
TiO_2	0.05
P_2O_5	0.93
CaO	8.44
MgO	6.47
Na_2O	0.62
K_2O	0.13
Loss on ignition	14.61

The rocks were broken up into small pieces and than washed several time by deionized water than the pieces were milled, the powder was soaked with deionized water for 24 hours, the powder was dried under 403K for 24 hours to remove physically adsorbed water. Particles of 90μm size were used in the research.

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3) Method:

a- Technique: UV technique was used to determine the absorption as function for concentration.the wavelengths of absorption were (279, 274, 271) nm for p-Chlorophenol , o-Chlorophenol and m-Chlorophenol respectively[9].

b- Equilibrium time: to determine required time for equilibrium between adsorbent and adsorbate, some certain concentration were mixed with 0.25g of SRP and they were put into thermostated shaker under 298K, samples were taken from the solution in different sequenced times to determine the change in the concentration with time passing, it was found out that the equilibrium time was half an hour.

c- Adsorption isotherms: 8 solutions (25ml each) of concentration (42-140)ppm from each compound were prepared. the solutions were mixed with 0.25g of SRP and than put in the shaker under different temperatures for half an hour.

The solutions then filtered and put into centrifuge for half an hour with 4000 rpm speed, finally the absorption was recorded by UV spectrophotometer (UV- 2100, double beam, Shimadzu).

Quantity of adsorbate in each case was calculated by the following equation[10]:

$$Q_e = \frac{V_{sol}/(C_o - C_e)}{m}$$

where: Q_e=quantity of adsorbate (mg/g)
V_{sol}=total volume of solution (L)
C_o=initial concentration of adsorbate solution (mg/L)
C_e= concentration of adsorbate solution at equilibrium (mg/L)
m= weight of adsorbent (g)

Results and discussion

1.Adsorption isotherms : the adsorbed quantity Qe for each equilibrium concentration was calculated as shown in Table (2).

Table (2)The value of adsorption of Chorophenol compound on SRP

Co	p-CP		o-CP		m-CP	
	Ce	Qe	Ce	Qe	Ce	Qe
45	33	1.2	34	1.1	38	0.7
59	47	1.3	47	1.3	52	0.7
73	59	1.4	58	1.5	65	0.8
87	68	1.9	69	1.8	77	1
101	79	2.2	82	1.9	89	1.2
115	87	2.8	96	1.9	102	1.3
129	98	3.1	109	2	115	1.4
143	106	3.7	120	2.3	125	1.8

Co and Ce are in (mg/L), Qe in (mg/g)
pH=7, T=298K

Qe Vs Ce was plotted to show the general scheme of adsorption isotherms as shown in figure (1)

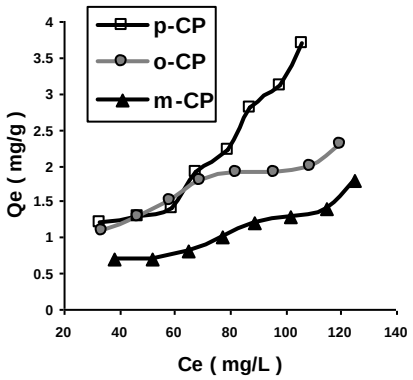

Figure (1) : Adsorption isotherms of Chlorophenol compounds on SRP (pH = 7 , T = 298 K)

The general scheme of adsorption isotherms of Chlorophenol compound on SRP surface pointing out that they were of (S) class according to Giles classification who depends on Freundlich principles for adsorption that can be found on heterogeneous surfaces, and if so that means there is possibility to have hydrogen bonds between solute and surface[11] .

Results showed that the adsorption of Chlorophenol compounds on SRP surface increasing as follows:

$$\text{p-Chlorophenol} \rangle \text{o-Chlorophenol} \rangle \text{m-Chlorophenol}$$

This sequence can be elaborated depending on solubility as the solubility

of Chlorophenol compounds in water increases as follows[12] :

m - Chlorophenol 〉 o - Chlorophenol 〉 p - Chlorophenol

This result agreement with Traube's rule By using linear application of Freundlich equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e$$

where KF, n= Freundlich constant

logQe Vs logCe was plotted as shown in figure(2) .Freundlich constant were calculate for Chlorophenol compounds as shown in Table(3).

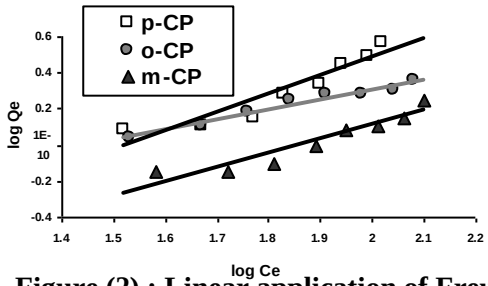

Figure (2) : Linear application of Freundlich equation

Table (3)The value of Freundlich constant (KF,n) for adsorption of Chlorophenol compounds on SPR

Compound	$K_F x_{10}^2$	n
p-CP	1.02	0.79
o-CP	18.41	1.91
m-CP	1.54	1.03

2.Effect of temperature: the adsorption was studied under different temperature (278, 298, 318) K , the results showed that adsorption of Chlorophenol compounds on SRP surface was endothermic process as shown in Table (4) and figure (3).

Table (4)Effect of temperature on adsorption of Cholorophenol on SRP

	p-CP						o-CP						m-CP					
	278K		298K		318K		278K		298K		318K		278K		298K		318K	
Co	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
45	35	1	33	1.2	32	1.3	37	0.8	34	1.1	34	1.1	40	0.5	38	0.7	38	0.7
59	48	1.1	47	1.3	44	1.5	49	1	47	1.3	45	1.4	53	0.6	52	0.7	51	0.8
73	61	1.2	59	1.4	56	1.7	62	1.1	58	1.5	54	1.9	66	0.7	65	0.8	64	0.9
87	70	1.7	68	1.9	65	2.2	76	1.1	69	1.8	67	2	79	0.8	77	1	75	1.2
101	82	1.9	79	2.2	71	3	89	1.2	82	1.9	76	2.5	92	0.9	89	1.2	87	1.4
115	95	2	87	2.8	77	3.8	103	1.2	96	1.9	87	2.8	106	0.9	102	1.3	98	1.7
129	107	2.2	98	3.1	88	4.1	116	1.3	109	2	99	3	119	1	115	1.4	110	1.9
143	116	2.7	106	3.7	95	4.8	128	1.5	120	2.3	108	3.5	130	1.3	125	1.8	119	2.4

Co and Ce are in (mg/L), Qe in (mg/g)

pH=7

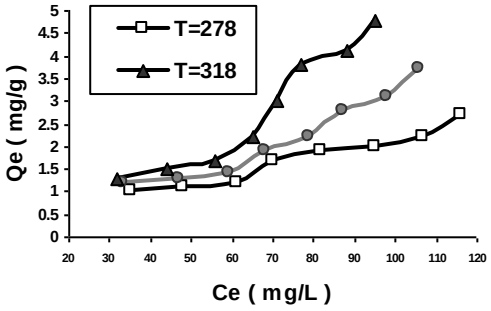

Figure (3) : Effect of temperature on adsorption of p-Chlorophenol on SRP at pH =7

By using Vant Hoff-Arrhenius equation:

$$\log X_m = \frac{-\Delta H}{2.303\,\mathrm{RT}} + cons\tan t$$

where Xm: maximum adsorbed quantity

R : gas constant

T: temperature

logXm Vs temperature was plotted as shown in figure (4) and Table (5), the values of ΔH were calculated as shown in Table (6).

Table (5)The values of temperature and (log Xm) for Chlorophenol compounds on SRP

	p-Chlorophenol		o-Chlorophenol		m-Chlorophenol	
T(K)	Xm(mg/g) When Ce=90(mg/L)	logXm	Xm(mg/g) When Ce=100(mg/L)	logXm	Xm(mg/g) When Ce=115(mg/L)	logXm
278	2	0.3	1.2	0.08	1	0
298	2.9	4.6	2	0.3	1.4	0.15
318	4.3	0.63	3.1	0.44	2.2	0.34

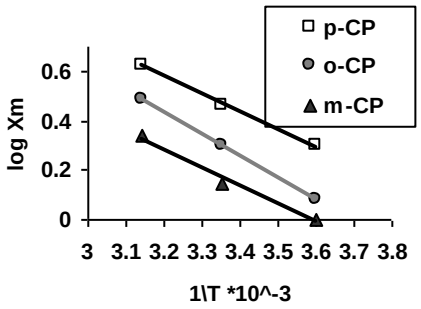

Figure (4) : Linear application of Vant Hoff-Arrhenius equation .

ΔS and ΔG values were calculated depending on following equations:

$$\Delta G = -RT\ In\frac{Q_e}{C_e}$$

$$\Delta G = \Delta H - T\Delta S$$

Table (6)The values of ($\Delta H, \Delta S, \Delta G$)of Chlorophenol compounds on SRP at 298

Compound	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/mol.K)
p-Chlorophenol	**12.42**	**2.03**	**34.85**
o-Chlorophenol	**10.13**	**2.31**	**26.24**
m-Chlorophenol	**13.68**	**2.61**	**37.14**

The positive values of ΔH and ΔG showed that there was absorption process took place simultaneously with the adsorption process, that means sorption process was taking place.

The positive values of ΔS proves that the adsorbed molecules were increasing randomly, the existence of the molecules in solution is less random than on surface.

Effect of pH: the adsorption was studied in different pH ranges (11, 7, 3) as shown in Table (7) and figure (5)

Table (7)Effect of pH on adsorption of Chlorophenol on SRP

	p-CP						o-CP						m-CP					
	pH=3		pH=7		pH=11		pH=3		pH=7		pH=11		pH=3		pH=7		pH=11	
Co	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe	Ce	Qe
45	31	1.4	33	1.2	34	1.1	33	1.2	34	1.1	35	1	38	0.7	38	0.7	41	0.5
59	44	1.5	47	1.3	47	1.2	45	1.4	47	1.3	47	1.2	50	0.9	52	0.7	53	0.6
73	55	1.8	59	1.4	60	1.3	58	1.5	58	1.5	60	1.3	63	1	65	0.8	66	0.7
87	61	2.6	68	1.9	70	1.7	63	2.4	69	1.8	72	1.5	74	1.3	77	1	78	0.9
101	68	3.3	79	2.2	81	2	76	2.5	82	1.9	85	1.6	85	1.6	89	1.2	92	0.9
115	75	4	87	2.8	90	2.5	85	2.9	96	1.9	98	1.7	92	2.3	102	1.3	105	1
129	85	4.4	98	3.1	102	2.7	97	3.2	109	2	112	1.7	105	2.4	115	1.4	118	1.1
143	92	5.1	106	3.7	110	3.3	105	3.8	120	2.3	125	1.8	115	2.8	125	1.8	130	1.3

Co and Ce are in (mg/L) Qe in (mg/g)

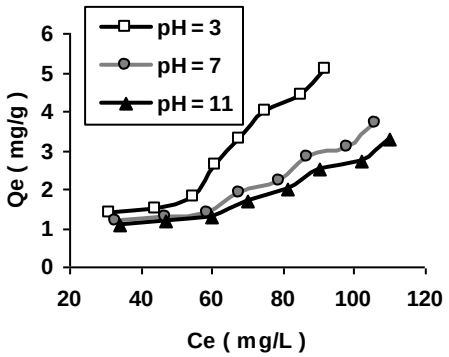

Figure (5) : Effect of pH on adsorption of p-Chlorophenol on SRP at T = 298 K.

The increasing of adsorption with the increase of acidity is attributed to that the surface of SRP is heterogeneous and contains negative charged group and positive charged group(13), but most of groups on the surface may be negatively charged, and in the acidic media the positive ions increase around hydroxyl group which lead to increasing electrostatic attract with negative group on the surface.

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دراسة قابلية الأمتزاز لمركبات كلوروفينول من محاليلها المائية على سطح مسحوق الصخور السليسية العراقية

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الخلاصة:

يتناول البحث دراسة قابلية الأمتزاز لمركبات كلوروفينول من محاليلها المائية على سطح مسحوق الصخور السليسية العراقية.

أستخدمت تقنية الأشعة فوق البنفسجية في تعيين ايزوثيرمات الأمتزاز وبينت النتائج أن ايزوثيرمات الأمتزاز تتبع معادلة فرندلش للامتزاز.

أوضحت النتائج أن عملية الأمتزاز من النوع الماص للحرارة أي أن زيادة درجة الحرارة تؤدي إلى زيادة قابلية الامتزاز، تم حساب (ΔH, ΔG, ΔS) لعملية الامتزاز.

بينت النتائج أن الامتزاز يزداد مع زيادة حامضية المحلول.