Effect of Temperature On The Dispersability Of The Grafted Acrylic Acid Onto Alumina Particles

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Abstract

The ability of different alumina-grafted particles was examined for adsorption of phenol and *p*-chlorophenol under different conditions (i.e. concentrations and temperatures). Dispersion stability of alumina in liquid medium (water) was studied using settling under gravity technique. The result shows the settling initial rate of the alumina-grafted acrylic acid particles was faster than initial rate of settling when alumina-graft acrylic acid monomer adsorbed phenol and *p*-chlorophenol and vice versa to the alumina-graft poly(acrylic acid) polymer.

Thermodynamic parameters values (ΔG, ΔS, ΔH) were calculated for adsorption processes of phenol and *p*-chlorophenol adsorbed onto different surfaces. The results revealed that positive and negative values were obtained implying that both endothermic and exothermic adsorption reactions may took place.

Key Words:Polymers,Polymers Adsorption,graft Alumina

Introduction

Adsorption of small molecules or polymeric materials onto solid surface plays an important role in a large number of practical applications, and provides good information about the physical and chemical properties of polymer in solution through their interaction with solid surface [1]. There are various factors that influence the adsorption process, such as chemical structure of the adsorbate, the nature of adsorbent, the solvent from which adsorption is made, and the type of anchoring groups [2].

In general when the concentration of adsorbate increases the capacity of adsorption increases [3]. In some cases, adsorption may be confined to only one layer of adsorbed molecules, i.e., only one molecule deep. Further adsorption ceases when the surface of the crystal lattice of adsorbent is covered [4]. The diagram representing the relationship between quantity adsorbed and the equilibrium concentration is called adsorption isotherm [5].

In physical adsorption, a decrease in temperature enhances the extent of adsorption. The decrease of adsorption with the increase of temperature implies by lechatelier's principle, that heat is evolved in the process of adsorption [6].

In chemisorptions, the quantity adsorbed may increase or decrease with rising temperature depending on the type of interaction and the bonding between the surface and the adsorbed molecules [7].

In most cases, chemisorptions require energy of activation. The amount of this energy is a function of type and the nature of adsorbate-adsorbent interaction and the concentration of adsorbate solution [8].

Natural water pollution by organic materials, such phenol and its derivatives which are the most harmful contamination, increases due to industrial activities and accidents.

In previous work, free radical polymerization was carried out onto alumina surface grafted with acrylic monomer. The later was chain extended by additional acrylic acid monomer in the presence of

benzoyl peroxide as initiator. The grafted monomer and polymer was characterized by different spectroscopic techniques, and was thermally analyzed [9].
In this paper,we studied the adsorption behavior to the standard alumina and to the compounds alumina-graft acrylic acid monomer and alumina-graft poly(acrylic acid)that we prepared at different temperatures and calculate thermodynamic parameters of the surface.

Experimental

Materials

Alumina,Alumina-grafted with acrylic acid monomer and Alumina-grafted poly(acrylic acid) polymer prepared and characterized as mentioned elsewhere[9].

Determination of maximum adsorption (λ_{max})

Ultra violet scanning spectrum of phenol and *p*-chlorophenol are recorded practically within the range (200-400) nm using (10 mm) width quartz . Wavelength values (λ_{max}) corresponding to the maximum absorbance for phenol and *p*-chlorophenol were (270nm) (280nm), respectively.
Many solutions of different concentrations were prepared by serial solutions of phenol and *p*-chlorophenol. Absorbance values of these solutions were measured at specific (λ_{max}) values for phenol and *p*-chlorophenol. In order to obtain the calibration curves of the (phenol and *p*-chlorophenol) solutions, the absorbency values plotted versus the concentration for both of them . The concentration range that falls in the region of applicability of Beer-Lambert's law was estimated and then used for subsequent determinations.
The amount of adsorbed phenol and *p*- chlorophenol was calculated from the initial and final concentration and the volume of solution. by the equation:-

$$Qe = \frac{V(C_o - C_e)}{m} \qquad \text{.........} (1)$$

Where:
Qe :quantity of adsorbate
V: volume of solution (ml).
C_o: initial concentration (mg/ml).
C_e: equilibrium concentration (mg/ml).

Adsorption uptake is expressed by the ratio (x/m) {also called Q_e which is defined as the quantity of adsorbate in (mg) held by (0.2) g of adsorbent} at certain conditions (temperature, pH). (Qe) values were plotted versus the equilibrium concentrations (C_e); the resulting diagrams are the adsorption isotherms that required for understanding and interpreting the systems under investigation [9].

Results and discussion

Studying the effect of temperatures on adsorption of phenol and *p*-chlorophenol were examined on the surfaces under study { standard alumina, alumina-graft acrylic acid monomer, and alumina-graft poly(acrylic acid)} at four temperatures (10, 25, 40, and 55) ºC .The results are listed in tables (1), (2) and (3)which, show the experimental data for all adsorbent surface
As shown form these tables, adsorption of phenol increased on the surfaces of alumina-grafted acrylic acid monomer and alumina-grafted poly (acrylic acid), when the temperature increased, while the adsorption of phenol decreased on the surfaces of standard alumina when temperature increased. On the other hand adsorption of *p*-chlorophenol on the surfaces was increased for standard alumina and alumina-graft poly (acrylic acid) as the temperature increased, and the adsorption decreased only on the surface of alumina-graft acrylic acid monomer when temperature increased.

Increasing the adsorption with increase temperature indicates that the adsorption is endothermic process; the molecules get a place on the crystal net work of the surface, and diffusion speed increase when temperature increases. These results include absorption and adsorption processes together and the dominant process is adsorption [10, 11].

The decrease in adsorption with the increase of temperature, the process is considered as an exothermic process, and that will be agreed with thermodynamic properties for adsorption [12].

Thermodynamic parameters

The enthalpy (ΔH) of adsorption of phenol and *p*-chlorophenol were calculated using the known thermodynamic equations [9]. The results are shown in table (4). Examining table (4) reveals quite clearly that the adsorption of phenol and *p*-chlorophenol on the surfaces of the materials under studying having both types of endothermic and exothermic processes.

The values of enthalpy (ΔH) of the phenol adsorption onto alumina particles surface, alumina-grafted acrylic acid monomer and alumina-grafted poly(acrylic acid) are negative. This implies that the adsorption process is exothermic, whereas positive values were obtained for (ΔH) indicating an endothermic type of adsorption for phenol onto alumina-grafted poly (acrylic acid).

The values of (ΔG) for all surfaces are positive this indicates that the adsorption process is non-spontaneous. Values of (ΔS) are negative and positive for surfaces adsorbate phenol and *p*-chlorophenol. The negative value gives proof that the adsorbate molecules may arrange themselves on the surface as consequence of binding, so that adsorbate molecules will be more regulate than in solution. But the positive value of (ΔS) means that adsorbate molecules are less regulate than in solution when absorption and adsorption processes are together [13].

The (ΔH) values of *p*-chlorophenol for standard alumina and alumina-grafted poly(acrylic acid) surfaces are positive and to the alumina-graft acrylic acid monomer is negative, but (ΔG) values for all surfaces are positive implies that adsorption process proceeds non-spontaneous.

(ΔS) Values to standard alumina, alumina-graft acrylic acid monomer, and to alumina-graft poly(acrylic acid) are negative. The above results lead to concede that the phenol molecules as adsorbate have better conformation onto different adsorbent surfaces comparing to the other adsorbed molecules, i.e. *p*-chlorophenol, this may explained in term of the size and polarity of the later adsorbate molecules.

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Table (1): The effect of temperature on adsorption of phenol and p-chlorophenol on Alumina surface

Phenol								
	10 ºC		25 ºC		40 ºC		55 ºC	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	86.07	0.696	86.12	0.694	89.09	0.545	88.37	0.581
125	106.77	0.911	106.81	0.909	109.92	0.754	108.86	0.807
150	123,07	1,346	122,56	1,372	128,61	1,069	125,15	1,242
175	152.91	1.104	152.90	1.105	150.84	1.208	156.30	0.935
200	184.20	0.790	182.99	0.850	168.71	1.564	175.09	1.245
225	184.66	2.017	188.41	1.829	200.88	1.206	194.16	1.542
250	210.42	1.979	221.90	1.405	221.93	1.403	228.47	1.076

***p*-Clorophenol**								
	10 ºC		**25 ºC**		**40 ºC**		**55 ºC**	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	75.74	1.213	92.63	0.368	91.20	0.440	89.66	0.517
125	99.37	1.281	117.13	0.393	114.13	0.543	112.34	0.633
150	120.39	1.480	136.40	0.680	133.74	0.813	134.31	0.784
175	105.51	3.474	148.27	1.336	127.54	2.373	124.00	2.550
200	126.58	3.671	172.87	1.356	144.54	2.773	136.43	3.178
225	138.74	4,313	192.16	1.642	150.47	3.726	146.76	3.912
250	153.02	4.849	213.16	1.842	182.74	3.363	172.98	3.851

Table (2): The effect of temperature on adsorption of phenol and *p*-chlorophenol on alumina-graft acrylic acid monomer surface

Phenol								
	10 ºC		25 ºC		40 ºC		55 ºC	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Q e(mg/g)
100	82.79	0.860	87.11	0.644	88.40	0.580	88.45	0.577
125	102.34	1.133	104.90	1.005	114.42	0.529	107.07	0.896
150	118.26	1.587	124.35	1.282	112.17	1.391	122.32	1.384
175	131.74	2.163	132.62	2.119	127.73	2.363	139.13	1.793
200	72.03	6.398	148.34	2.583	173.98	1.301	173.13	1.343
225	83.43	7.078	184.99	2.000	183.54	2.073	174.32	2.534
250	102.28	7.386	204.08	2.295	202.01	2.399	187.14	3.143

p-Clorophenol								
	10 ºC		25 ºC		40 ºC		55 ºC	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	84.27	0.786	78.93	1.053	88.59	0.570	88.33	0.583
125	102.20	1.138	100.52	1.224	107.16	0.892	110.89	0.705
150	123.08	1.346	121.69	1.415	132.40	0.880	134.06	0.797
175	136.51	1.924	113.82	3.059	132.34	2.133	148.87	1.306
200	141.14	2.943	137.94	3.103	162.23	1.888	171.49	1.425
225	149.71	3.764	154.34	3.533	166.98	2.901	198.89	1.305
250	176.23	3.688	180.36	3.481	195.45	2.727	199.65	2.517

Table (3): The effect of temperature on adsorption of phenol and *p*-chlorophenol on polymer (A) surface

Phenol								
	10 ºC		25 ºC		40 ºC		55 ºC	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	94.90	0.255	79.50	1.025	78.94	1.053	72.98	1.351
125	118.14	0.343	102.93	1.103	104.02	1.049	97.60	1.370
150	127.91	1.104	115.21	1.739	117.32	1.634	110.90	1.955
175	130.34	2.233	120.49	2.725	129.29	2.285	111.29	3.185
200	173.70	1.315	166.56	1.672	156.22	2.189	149.98	2.501
225	178.38	2.331	200.20	1.240	186.34	1.933	171.06	2.697
250	209.17	2.041	202.72	2.364	202.42	2.379	191.77	2.911

p-Clorophenol								
	10 ºC		25 ºC		40 ºC		55 ºC	
Co (mg/L)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)	Ce (mg/L)	Qe (mg/g)
100	80.56	0.972	82.00	0.900	84.21	0.789	77.30	1.135
125	95.22	1.489	98.49	1.325	102.08	1.146	101.82	1.159
150	114.00	1.800	121.81	1.409	123.61	1.319	118.89	1.555
175	130.16	2.242	127.80	2.360	137.83	1.858	134.75	2.012
200	142.91	2.854	148.13	2.593	150.38	2.481	141.09	2.945
225	178.54	2.323	167.69	2.865	173.45	2.577	152.69	3.615
250	205.45	2.227	188.73	3.063	183.65	3.317	174.23	3.788

Table (4): Thermodynamic data to adsorption phenol and *p*-chlorophenol at the surfaces under study at 25 °C

Surfaces	Phenol			*p*-Clorophenol		
	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/mol.K)	ΔH (KJ/mol)	ΔG (KJ/mol)	ΔS (J/mol.K)
Standard Alumina	-6.466	11.982	-0.062	28.268	11.642	0.056
Alumina-grafted acrylic acid monomer	-78.512	11.345	-0.301	-15.872	9.819	0.020
Alumina-grafted poly(acrylic acid)	10.392	12.470	0.003	9.238	10.105	-0.003

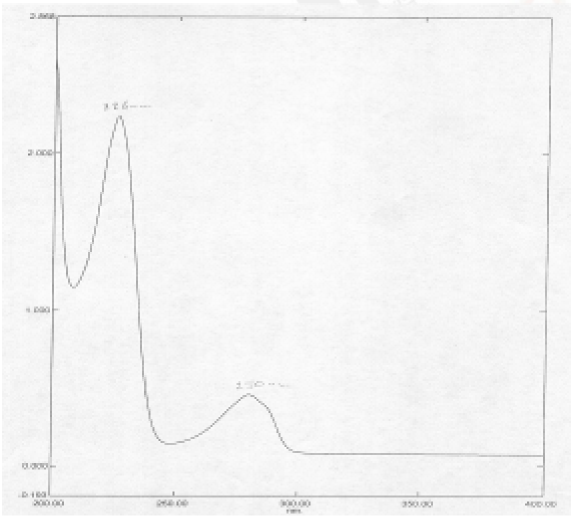

Fig. (2): Scanning spectrum of *p*-chlorophenol

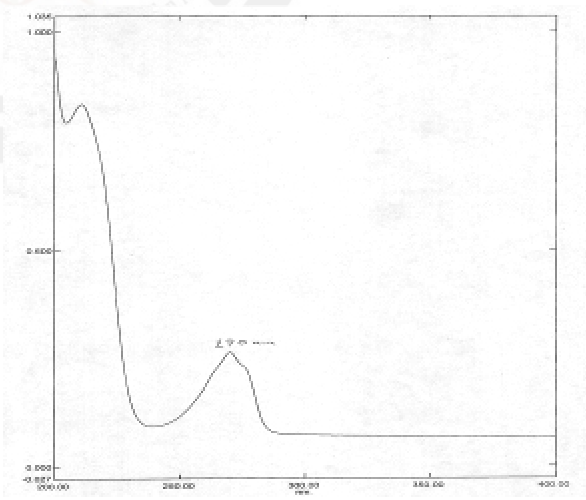

Fig.(1):Scanning spectrum of phenol

تأثيرالتغيير في درجات الحرارة على انتشارية حامض الاكريلك المطعم بين جزيئات الالومينا

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الخلاصة

تم في هذه الدراسة اختبار قابلية سطوح جسيمات الألومينا ، الألومينا المطعمة بمونمر حامض الأكريلك و الألومينا المطعمة ببولي (حامض الأكريلك) لأمتزا ز جزيئات الفينول وبارا-كلوروفينول تحت ظروف مختلفة من درجات الحرارة .
وتم حساب الدوال الثرموديناميكية ($\Delta H, \Delta S, \Delta G$) لعملية امتزاز الفينول والبارا-كلورو فينول على السطوح قيد الدراسة وأظهرت النتائج قيم موجبة وأخرى سالبة دلالة على حدوث عمليات امتزاز محبة للحرارة وأخرى باعثة للحرارة.

الكلمات المفتاحية:البوليمرات،امتزازالبوليمرات،الالومينا المطعم