ADSORPTION CAPACITY OF CARBON SOOT FOR CHROMIUM (VI) AND COPPER (II) FROM THEIR SOLUTIONS INSTEAD OF PAC

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Elimination of Chromium (Cr^{6+}) and Copper (Cu^{2+}) from waste drain water is of great importance for the environment. Some industrial activities such as leather tanneries and electroplating pump huge amounts of water contaminated with toxic heavy metals. They should be of special interest in the field of industrial waste water treatment; adsorption is one of the most important methods used for toxic heavy metals elimination. Carbon soot that produced as a byproduct from the partial oxidation of natural gas has been utilized as an alternative and low cost adsorbent instead of costly expensive powdered activated carbon (*PAC*). The adsorption data showed that the removal of Cr^{6+} and Cu^{2+} decreases as the temperature increases. The enthalpy of adsorption was determined by fitting results to Van't Hoff equation, revealing that the adsorption is exothermic and this supports the lowering of adsorption capacity with the temperature. The study succeeded in providing an alternative and low cost adsorbent and can be utilized with appropriate efficiency.

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1. Introduction

Wastewater produced from many industries contains a significant amount of heavy metal ions. They are considered uneco-friendly materials cause living organisms destruction. The effluents of several industrial activities contain different heavy metals ions. Leather tanneries and electroplating industries are the common industries which pumping huge amounts of Chromium and Copper ions into the waste drain water. They are continuously being discharged into the ecosystem and are environmentally toxic. The excess copper compound in the body may affect aging, schizophrenia, mental illness, Indian childhood cirrhosis and Alzheimer's diseases [1, 2]. Copper is harmful to marine life since it damages the gills, liver, kidneys, and the nervous system and change the reproductive system of fish[3]**.** Chromium does not undergo biodegradation. The accumulation of Chromium at high levels may generate serious problems and can ultimately become lethal [4]. Adsorption is the most effective and widely used technique for the removal of heavy metals from wastewater. Due to the high cost of activated carbon, efforts are being directed to find effective alternatives and low cost adsorbent materials. Many different adsorbents have been used for removing heavy metal ions; for example carbon from Banana peels [5]. Activated carbon prepared from coconut tree sawdust was used as adsorbent[6], fly ash[7], Kaolinite[8] and Bentonite [9]. Between these alternatives Carbon soot was used as a cheap adsorbent material[10]. The main objective here is to evaluate the removal of chromium and copper by adsorption on

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carbon soot as a cheap adsorbent material instead of *PAC* and estimating the enthalpy of adsorption for the process.

2. Experimental

2.1. Adsorbent materials

Carbon soot was produced as a byproduct from the partial oxidation of natural gas at El-Delta Company for Fertilizers and Chemical Industries, Egypt. Carbon soot is considered a solid waste and used for many adsorption studies as a low cost alternative adsorbent material; *PAC* was supplied from El-Nasr Co. for Pharmaceutical Industry, Egypt. Both of adsorbents were analyzed and their characteristics in previous work[11].

2.2. Heavy metal solution

Solutions of Chromium (Cr^{6+}) and Copper (Cu^{2+}) were prepared by dissolving Cr $(NO_3)_6$ and $Cu(NO_3)_2$, respectively in distilled water. All chemicals used were of the highest analytical grade.

2.3. Analytical procedures

Determination of heavy metal ions in their solution mixture was carried out by Spectro Genesis FEE, Inductively Coupled Plasma-atomic emission spectrometry (ICP), Germany. Analytical procedures analyses were according to methods for the examination of water and waste water[12].

2.4. Experimental procedures

In a series of glass vials put different doses of adsorbent e.g., 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 g per 25 ml of a mixture of heavy metal ions solution (100 ppm of each). The vials are sealed and shaken at specified conditions. After that, the adsorbent was filtered off and the remaining concentrations of Cr^{+6} and Cu^{+2}were determined; the process repeated at different temperatures.

3. Results and discussion

Firstly the optimum conditions for the adsorption heavy metal ions were determined; it was found that the removal of Cr^{+6} was 38.6% and 26.5% on *PAC* and carbon soot respectively. Also, the removal of Cu^{+2} is 77.9% and 65.2% on *PAC* and carbon soot respectively. The behavior of adsorption processes was discussed through plotting data to both Langmuir and Temkin isotherms.

3.1. Langmuir isotherm

Langmuir model assumes that uptake of heavy metal ions occurs on a homogenous surface by forming a monolayer without any adsorbent-adsorbate interactions.

$$\frac{1}{x/m} = \frac{1}{b} + \frac{1}{ab}\left(\frac{1}{C}\right) \tag{1}$$

Where, *C* is the equilibrium concentration, *x/m* is the amount of ions adsorbed per adsorbent (mg / g), *a* is the Langmuir constant and *b* is the monolayer coverage constant. Plotting of *1/*(*x/m*) against (*1/C*) as shown in Figs. 1-4. From slopes (*1/ab*) and intercepts (*1/b*) of these linear plots, Langmuir constants were calculated and listed in Table 1. From previous data it is found that the monolayer coverage (*b*) values in case of *PAC* are higher than that of the carbon soot; this interprets the higher adsorption capacity in case of using PAC. This in agreement with the findings in literatures which indicate that the increase in *b* value with the decreasing in the particle size of adsorbent [13]. Results also show that, the monolayer coverage parameter generally decreases with increasing temperature and this may attributed to an exothermic process. Values of monolayer coverage (*b*)in case of Cu^{+2}adsorption are higher than Cr^{+6} adsorption and this explain the higher adsorption capacity for Cu^{+2} than Cr^{+6}; this may due to lower ionic radii for Cu^{+2}.

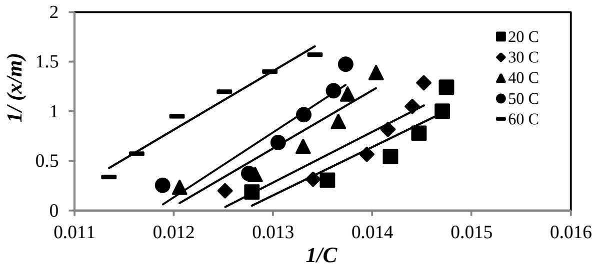

Fig. 1. Langmuir plots for adsorption of Cr^{+6}on carbon soot at different temperatures

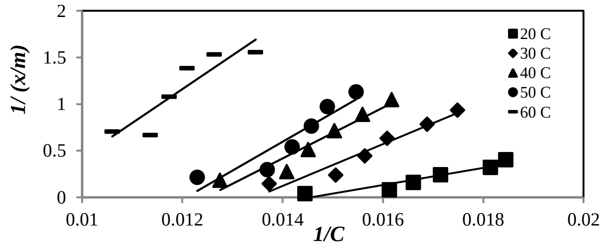

Fig. 2. Langmuir plots for adsorption of Cr^{+6} on PAC at different temperatures.

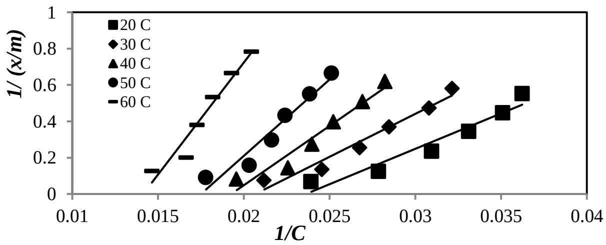

Fig. 3.Langmuir plots for adsorption of Cu^{+2} on carbon soot at different temperatures

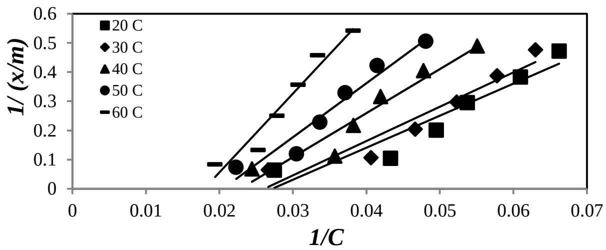

Fig. 4.Langmuir plots for adsorption of Cu^{+2} on PAC at different temperatures.

Table 1.Langmuir constants for adsorption of Cr^{+6}andCu^{+2}on carbon soot and PAC.

Heavy metal ion	Temp.(°C)	Carbon soot				PAC			
		a	***b***	R_L	R^2	***a***	***b***	R_L	R^2
Cr^{+6}	20	0.0011	0.162	0.901	0.842	0.0015	0.748	0.869	0.903
	30	0.0016	0.157	0.862	0.828	0.0013	0.332	0.885	0.943
	40	0.0012	0.143	0.892	0.879	0.0012	0.295	0.892	0.925
	50	0.0012	0.159	0.892	0.855	0.0012	0.268	0.892	0.861
	60	0.0013	0.159	0.885	0.969	0.0018	0.312	0.556	0.817
Cu^{+2}	20	0.024	1.08	0.249	0.933	0.0272	3.352	0.269	0.899
	30	0.021	1.02	0.323	0.961	0.0262	3.248	0.276	0.915
	40	0.019	0.793	0.345	0.948	0.0302	2.073	0.249	0.923
	50	0.017	0.683	0.370	0.947	0.0204	2.645	0.294	0.947
	60	0.014	0.574	0.417	0.948	0.0179	2.073	0.358	0.951

3.2. Temkin isotherm

Temkin isotherm assumes that, heat of adsorption molecules or ions layer decreases linearly with coverage due to adsorbent-adsorbate interactions, and that the adsorption is characterized by a uniform distribution of bonding energies, up to some maximum binding energy; Temkin isotherm is represented by the following equation [9].

$$q_e = (RT/b_T) \ln K_T + (RT/b_T) \ln C_e \qquad (2)$$

Where, q_e is the amount of ions adsorbed per adsorbent (x/m),T is the absolute temperature (K), R is the universal gas constant ($R = 8.314$ J/K. mol), K_T is the equilibrium binding energy constant (L/mg) and b_T is the variation of adsorption energy (KJ/mol). By plotting of q_e against lnC_e give a group of straight lines as shown in Figs. (5-8).From slopes (RT/b_T) and intercepts (RT/b_T)(lnK_T) of these straight lines all Temkin parameters were calculated and listed in Table 2.From these results, it is found that, the lower values of both adsorption energy change (b_T) and equilibrium binding energy constant (K_T, L/mg) indicate a physical adsorption[9].Values of variation of adsorption energy (b_T) increase with increasing temperature, this makes the adsorption process to be more difficult as the temperature increase. Values of the equilibrium binding energy (K_T) decrease with increasing temperature; this means the adsorbent-adsorbate interaction decreases as the temperature increases and desorption occur at higher temperatures, this lower the removal percent at high temperatures [9].

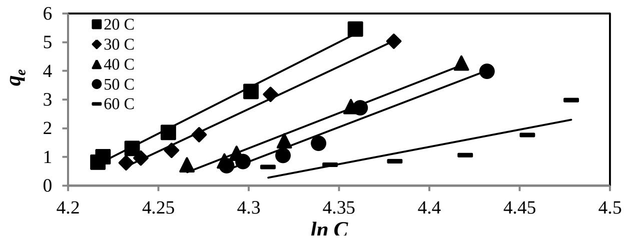

Fig. 5.Temkin plots for adsorption of Cr^{+6} on carbon soot at different temperatures

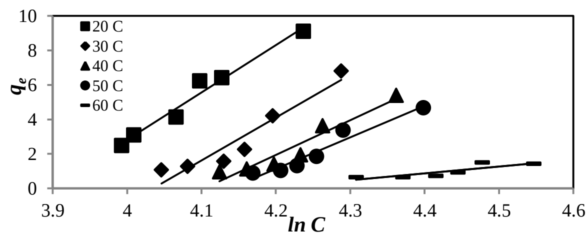

Fig. 6.Temkin plots for adsorption Cr^{+6} on PAC at different temperatures

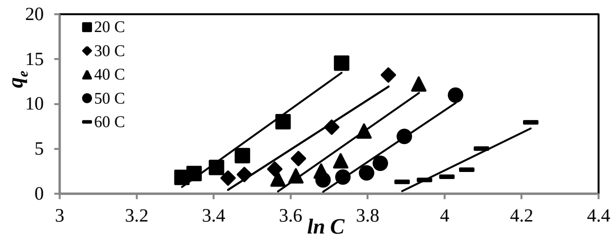

Fig. 7.Temkin plots for adsorption of Cu^{+2} on carbon soot at different temperatures.

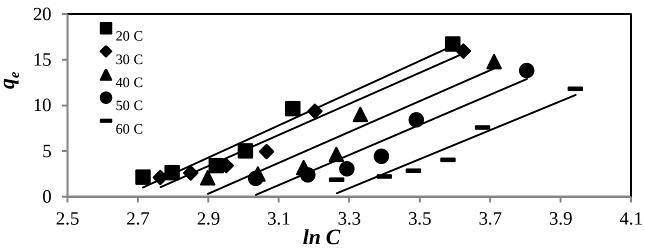

Fig. 8.Temkin plots for adsorption of Cu^{+2} on PAC at different temperatures.

Table 2.Temkin constants for adsorption of Cr^{+6}andCu^{+2}on carbon soot and PAC.

Heavy metal ion	**Temp.(^{o}C)**	**Carbon soot**			**PAC**		
		b_T **(J/mol)**	K_T **(L/mg)**	R^2	b_T **(J/mol)**	K_T **(L/mg)**	R^2
Cr^{+6}	20	76.22	0.0151	0.993	88.78	0.748	0.972
	30	85.19	0.0149	0.994	101.58	0.332	0.912
	40	105.91	0.0143	0.985	129.40	0.295	0.922
	50	111.48	0.1410	0.961	146.51	0.268	0.938
	60	229.95	0.0137	0.748	687.84	0.312	0.744
Cu^{+2}	20	79.37	0.0371	0.955	138.17	0.0701	0.965
	30	90.91	0.0326	0.925	147.92	0.0670	0.971
	40	86.71	0.0285	0.923	154.16	0.0561	0.903
	50	93.34	0.0253	0.924	163.05	0.0487	0.911
	60	132.34	0.0210	0.893	174.64	0.0391	0.921

3.3. Adsorption thermodynamics

Van't Hoff equation determines if the adsorption was endothermic or exothermic [8, 13]. Van't Hoff equation written as below, where ΔH^o is the enthalpy of adsorption and ΔS^o is the entropy change and *Kc* is the equilibrium constant.

$$LnK_c = \Delta S^o/R - (\Delta H^o/R)\ 1/T \quad (3)$$

By plotting of lnK_c versus *1/T* (figures 9 and 10) and enthalpy of adsorption (ΔH^o) were calculated from slopes of straight lines ($\Delta H^o/R$)and listed in Table 3.Negative sign of enthalpy indicates that the adsorption processes were exothermic and this explains the decreasing of adsorption capacity with increasing temperature [8,11, 13]). It's also found that enthalpy of adsorption in case of carbon soot is highly exothermic than that in case of *PAC*, this explain the lower removal efficiency in case of carbon soot when compared with *PAC*.

Table 3.Enthalpy change for adsorption of Cr^{+6} and Cu^{+2} on carbon soot and PAC.

Heavy metal ions	ΔH^o (J / mol)	
	Cr^{+6}	Cu^{+2}
Carbon soot	- 339.294	- 440.476
PAC	- 65.814	- 149.569

4. Conclusions

Carbon soot can be used as alternative low cost adsorbent with very good removal efficiency in comparison to PAC.

Langmuir plots for the adsorption process indicate that, monolayer coverage decreases with increasing temperature. This explains the decreasing of adsorption with increasing temperature and the adsorption processes were of physical adsorption type.

Temkin isotherm indicates that the adsorbent-adsorbate interaction decreases as the temperature increases and this explain why adsorption of Cr^{+6} and Cu^{+2} decreases at high temperatures.

The enthalpy of adsorption on carbon soot and *PAC* is exothermic. This also interprets the decreasing of adsorption capacity with increasing temperature.

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