Adsorption of Copper from Copper Acetate and Copper Chloride Solutions on Carbon Black "Spheron 9"---III

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Summary: Adsorption studies of copper from copper acetate and copper chloride solutions on carbon black "Spheron 9" were made at three different pH ranges. Adsorption of copper increased with increase in pH, which was attributed mainly to excessive precipitation and formation of unionized or partially ionized copper species at high pH, which might have adsorbed to a greater extent on the nonpolar graphitic surface of carbon compared to ionic species. Effect of anion of the copper salt was also observed to have an effect on adsorption. Fruendlich's and Langmuir's equations were applied to the adsorption isotherms and it was found that both equations were obeyed.

Introduction

Use of activated carbon as an adsorbent for removal of organics and inorganics from water [1-3], recovery of precious metals [4-5] and as a support for inorganic catalysts [6] is well documented. Extensive work has been reported in the literature on the adsorption of inorganics from water by activated carbon, however, data on the use of carbon black for the adsorption of inorganics is limited and needs attention. Carbon black is a relatively nonporous carbonaceous material compared to activated carbon and may avoid the effect of microporousity in giving a true explanation to the adsorption behaviour. Work on adsorption of copper from copper sulfate solution on carbon black "Spheron 9" at different pH in the authors laboratory [7] revealed that pH had a predominant effect on the adsorption of copper. Effect of pH on adsorption of various metals from their salt solution on activated carbon and related material has also been investigated by earlier workers [2,8-10] and increase in adsorption with increase in pH has generally been observed.

The present work will be directed to investigate the effect of pH on the adsorption of copper on carbon black "Spheron 9" from copper salt solutions having different anions such as copper acetate and copper chloride. The idea is to know whether adsorption of copper is mainly affected by solubility of the copper salt and its hydrolysed species at high pH or anion of the salt itself play some contributing role. Copper from Copper acetate is expected to be adsorbed to greater extent compared to that from copper chloride as well as copper sulfate [7] at any pH due to its low solubility and low ionization. Effect of the anion of cadmium salt i.e., Cl^-, NO_3^- and SO_4^{2-} on adsorption of cadmium by activated carbon has been investigated by Dobrowolski *et al.* [11]. They found that adsorption depends primarily on the

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type of anion, decreasing in the order $NO_3^- > Cl^- > SO_4^{2-}$.

Results and Discussion

The adsorption isotherms of copper from copper acetate solution at the pH ranges 2.3-2.4, 5.2-5.5 and 6.2-7.0 and from copper chloride solution at the pH ranges 2.3-2.4,4.2-5.4 and 6.2-6.9 are shown in Fig. 1 and Fig. 2 respectively. These figures show that increase in pH results in an increase in adsorption of copper over the whole concentration range from both salt solutions. The adsorption isotherms at the highest pH ranges of 6.2-7.0 in Fig. 1 and 6.2-6.9 in Fig. 2 show quite high adsorption compared to that at the lower pH ranges. High adsorption at the high pH ranges was thought to be due to the presence of copper predominantly in the unionized or partially ionized hydrolyzed species such as $Cu(OH)_2$ and Cu^+ (OH) at high pH, which would have adsorbed to a greater extent on the nonpolar carbon surface compared to adsorption of Cu^{2+}, Cu^{2+} was thought to be present predominantly at low pH. It can also be noticed that adsorption at the highest pH range of 6.2-7.0 in Fig. 1 and 6.2-6.9 in Fig. 2 with blank correction is significantly low compared to that of the uncorrected (without blank correction) isotherms. This observation was also noticed in our previous studies of adsorption of copper from copper sulfate solution [7], which was explained to be due to excessive precipitation at the high pH ranges as noted by the appearance of turbidity in the blank salt solution. Thus in the blank corrected isotherms, the blank solutions were also filtered to remove the precipitated copper so as to avoid its inclusion in the calculation for isotherm determination. The uncorrected isotherm is not indicative of true adsorption rather it shows apparent adsorption, which is a combination of true adsorption as well as precipitation. True adsorption isotherms of copper from copper acetate solution at the pH range 6.2-7.0 (with blank correction) and from copper chloride at the pH range 6.2-6.9 (with blank correction), have reduced considerably compared to that of apparent adsorption at the same pH ranges (without blank correction), however, they are still high compared to adsorption isotherms at lower pH ranges. This indicates that increase in pH has a positive effect on adsorption of copper, which is quite significant in case of copper acetate. Copper acetate, which is comparatively less soluble shows more adsorption than that from
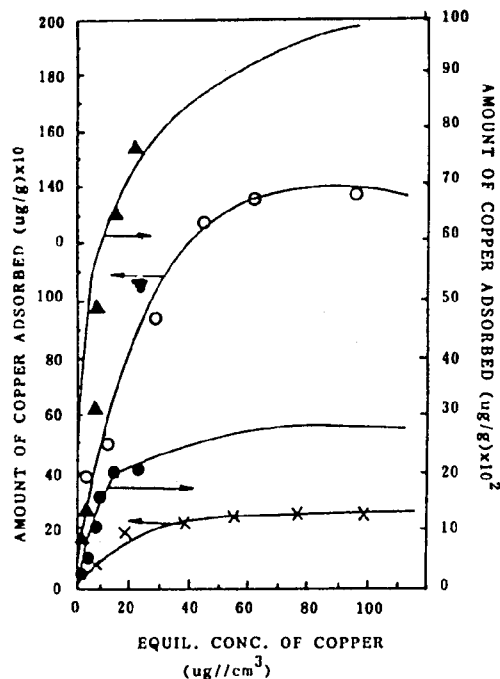

Fig. 1: Adsorption isotherms of copper from copper acetate solutions at different pH ranges. Carbon dosage: 0.5 g; pH ranges: x, 2.3-2.4; 0, 5.2-5.5; • 6.2-7.0 (With Blank Correction); Δ, 6.2-7.0 (Without Blank Correction).

relatively more soluble copper chloride at the two higher pH ranges. Adsorption at the lowest pH ranges from both the salts do not show any significant difference. Low adsorption at low pH ranges might be due to more dissociation of the copper salt into ionic species, which would be adsorbed to a lesser extent compared to that of undissociated metal species, because large fraction of the carbon surface is composed of the non polar basal graphitic plane area, which would adsorb non polar or unionized species in preference to those of the polar or ionic species. Another factor responsible for low adsorption at the acidic pH range, might be due to competition between H^+ and the copper cations for negative sites situated at the edge plane area of the microcrystallite on the surface of carbon particles. This would apparently favour more hydrogen ions adsorption compared to copper cations. Both the edge plane and basal plane areas of microcrystallites situated in the interior of the carbon particles may not be exposed to the adsorbing species due to the relatively nonporous
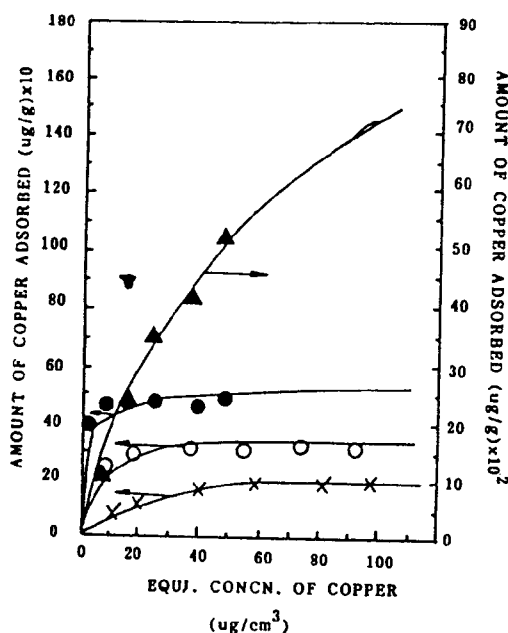
Fig.2: Adsorption isotherms of copper from copper chloride solutions at different pH ranges. Carbon dosage: 0.5 g; pH ranges : x, 2.3-2.4; 0, 4.2-5.4; ● , 6.2-6.9 (With Blank Correction); Δ, 6.2-6.9 (Without Blank Correction).

nature of carbon black "Spheron 9". Effect of pH on adsorption of Sr^{2+} on activated carbon has also been studied by Mata - Arjona et al. [12]. They found that adsorption was strongly affected by pH of the medium, which was though to be due to competition between Sr^{2+} and H^+ for active sites on the surface of carbon. Increased adsorption of copper from copper sulfate solution at the pH range 6.7-7.1 was also observed in our earlier work [7], which was also ascribed to be due to the above mentioned factors. Other investigators [10] also observed increased adsorption of metals at the conditions which retard ionization.

The linear from of Fruendlich's equation ln (x/m) = lnK + 1/n ln C was applied to the adsorption isotherms of Fig. 1 and the resulting Fruendlich's isotherms have been given in Fig. 3, which show that the adsorption isotherms obey Fruendlich's equation. As has been mentioned before that at pH 6.2-7.0 excessive precipitation of copper occurs, therefore Fruendlich's equation was applied to the blank corrected isotherm at pH 6.2-7.0 to avoid the inclusion of precipitated copper.
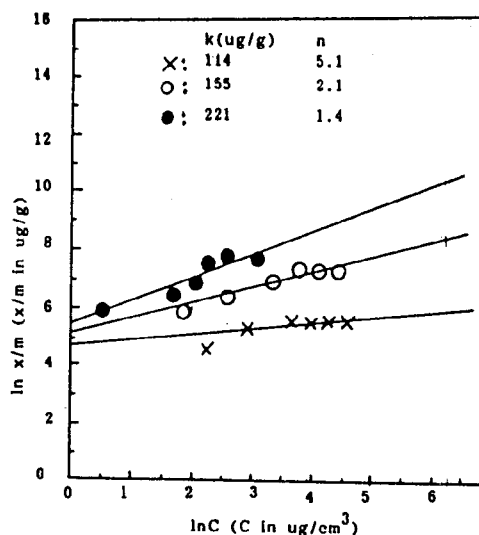

Fig.3: Fruendlich's isotherms of copper from copper acetate solutions at different pH ranges. Carbon dosage: 0.5 g ; x, 2.3-2.4; 0, 5.2-5.5; ● , 6.2-7.0 (With Blank Correction).

The values of K, which is a measure of the adsorption capacity of the adsorbent at unit concentration are 114 (µg/g), 155 (µg/g) and 221 (µg/g) at the pH ranges 2.3-2.4, 5.2-5.5 and 6.2-7.0 (blank corrected) respectively, which indicates increase in adsorption with increase in pH of the medium. The values of n which is the inverse of slope 1/n and indicates variation of adsorption with concentration are 5.10, 2.10 and 1.40 at the pH ranges 2.3-2.4, 5.2-5.5 and 6.2-7.0 respectively. This shows that increase in adsorption with increase in concentration is lowest and highest at the pH ranges 2.3-2.4 and 6.2-7.0 respectively.

Fruendlich's equation has also been applied to the adsorption isotherms of copper from copper chloride solution (Fig. 2) and the resultant linear form of Fruendlich's isotherm has been given in Fig. 4. The values of adsorption capacity K are 49, 230 and 380 µg/g at the pH ranges 2.3-2.4, 4.2-5.4 and 6.2-6.9 (with blank correction) respectively, showing minimum and maximum adsorption at the lowest and highest pH ranges. The values of K at the two higher pH ranges are high compared to their values from copper acetate solution, whereas the value of K at the lowest pH range is low compared to its value from copper acetate solution.
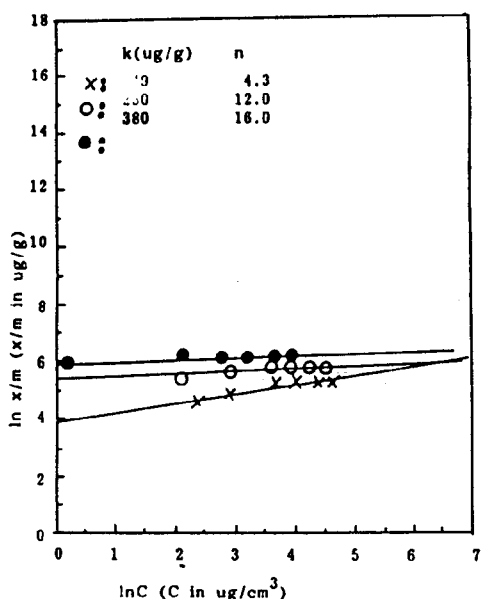
Fig.4: Fruendlich's isotherms of copper from copper chloride solutions at different pH ranges. Carbon dosage: 0.5 g ; x, 2.3-2.4; 0, 4.2-5.4; • , 6.2-6.9 (With Blank Correction).

The values of n are 4.3, 12.0 and 16.0 at the pH ranges 2.3-2.4, 4.2-5.4 and 6.2-6.9 respectively. The quite high values of n, at the two higher pH ranges indicate that change in adsorption with increase in concentration of the solution is quite small at the pH ranges 4.2-5.4 and 6.2-6.9. The value of n at the pH range 2.3-2.4, even though is comparatively small, does not show appreciable increase in adsorption with increase in concentration.

Langmuir's equation $C/(x/m) = 1/ab + C/b$ was also applied to the adsorption isotherms of Fig. 1 and Fig. 2 and the resultant Langmuir's isotherms have been plotted in Fig. 5 and Fig. 6 for copper acetate and copper chloride respectively. It can be seen that adsorption from both the salt solutions obey Langmuir's equation at all pH ranges. Adsorption from copper acetate solution at the pH range 6.2-7.0 (without blank correction) and from copper chloride at the pH range 6.2-6.9
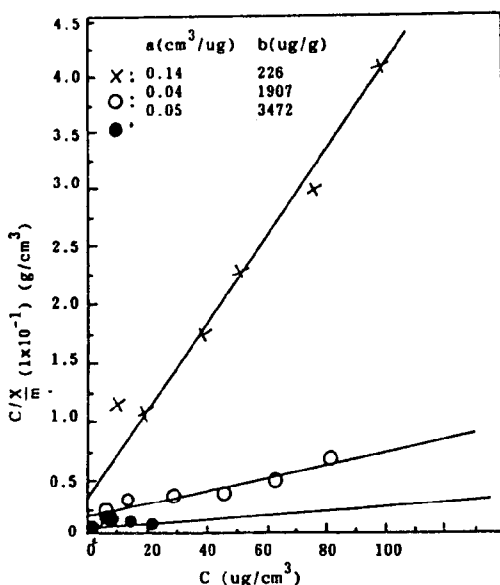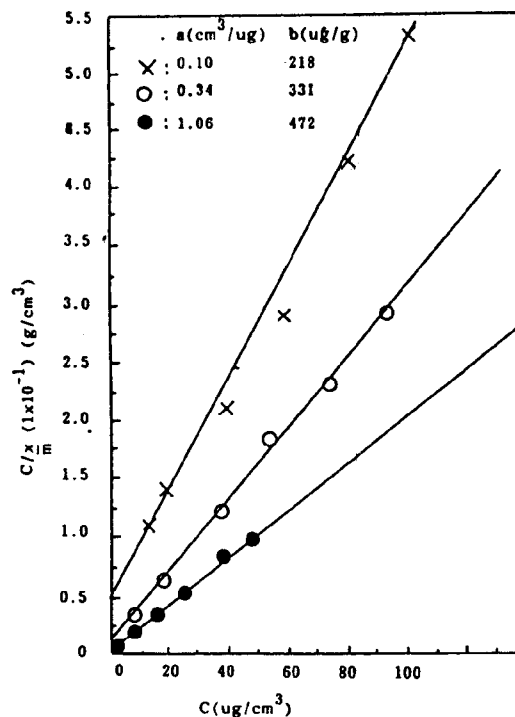

Fig.5: Langmuir's isotherms of copper from copper acetate solutions at different pH ranges. Carbon dosage: 0.5 g; x, 2.3-2.4; 0, 5.2-5.5; • , 6.2-7.0 (With Blank Correction).

Fig.6: Langmuir's isotherms of copper from copper chloride solutions at different pH ranges. Carbon dosage: 0.5 g; x, 2.3-2.4; 0, 4.5-5.4; • , 6.2-6.9 (With Blank Correction).

(without blank correction) do not obey Langmuir's equation due to excessive precipitation and were thus not reported. The value of b which is the amount of copper adsorbed/gram of adsorbent when the adsorbent is covered by a monolayer of copper are 226, 1907 and 3472 μg/g at the pH ranges 2.2-2.4, 5.1-5.5 and 6.2-7.0 from copper acetate solution and 218, 331 and 472 μg/g at the pH ranges 2.3-2.4, 4.2-5.4 and 6.2-6.9 from copper chloride solution respectively. The quite large values of b at the two higher pH ranges from copper acetate solution indicates higher monolayer adsorption compared to that from copper chloride solution as well as from copper sulfate solution in our earlier studies [7].

The high adsorption of copper acetate might be due to low solubility and ionization of copper acetate salt compared to that from copper chloride and copper sulfate. Copper chloride which is the most soluble of the three salts was expected to show the lowest adsorption, however, it was observed from the adsorption isotherms of the three salts that copper chloride show higher adsorption compared to that of copper sulfate at the higher pH range, which might be due to the fact that anion of the salt has some additional effect beside solubility and ionization.

Experimental

Adsorption of copper from copper acetate and copper chloride solutions at different pH ranges

Carbon black "Spheron 9" obtained from Cabot Corporation was used in the present investigation. The carbon was extracted with benzene in Soxhlet apparatus for 24 hrs. and then dried at 100°C in a vacuum oven. Surface area was determined by Snow,s. Iodine adsorption method, which was found to be 66m²/g. Surface area by liquid nitrogen adsorption was 116 m²/g [13]. The ash content found by earlier investigators was negligibly small i.e., below 0.1 % containing mainly iron and silica. The surface functional groups are mainly carboxylic, phenolic, quoinonic and lactonic types [14].

50 cm³ portions from copper acetate and copper chloride salt solution of concentration ranges from 10 to 100 μg/cm³ copper were introduced into erlenmeyer flasks containing 0.5 g portion of carbon black. pH was adjusted with 0.1

M NaOH and 0.1 M HCl solutions. The flasks were stirred for 2 hrs. at 35 ± °C. The slurries were then filtered through ordinary filter paper discarding the first 5 cm³ portions of filtrates. 10 cm³ portions of the clear filtrate were then titrated with 0.001 M EDTA solution using murexide as indicator [15]. Blank determination were made simultaneously alongwith samples under the same set of experimental conditions. Each determination was performed in triplicate. The % cofficient of variation of copper adsorption from copper acetate solutions was calculated and found to be 1.67, 1.62, 1.65 (with blank correction) and 1.76 (without blank correction) at pH ranges 2.3-3.2.4, 5.2-5.5 and 6.2-7.0 respectively. From copper chloride it was found to be 1.72, 1.77, 1.75 (with blank correction) and 1.80 (without blank correction) at pH ranges 2.3-2.4, 4.2-5.4 and 6.2-6.9 respectively.

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