

Removal of Copper from Aqueous Solution Using Orange Peel, Sawdust and Bagasse

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Abstract

Orange peel, sawdust and bagasse have been used as adsorbents for the removal of Cu(II) from aqueous solution. The effects of contact time, pH, concentration, dose and ionic strength on the removal of Cu(II) have been studied. Moreover, treated sawdust has been used as an adsorbent for the same. The equilibrium adsorption capacity of the adsorbents for Cu(II) was obtained by Langmuir isotherm. The ionic strength effect on the removal of Cu(II) from its aqueous solution indicated that the removal followed ion-exchange mechanism.

Keywords: Removal; Adsorption; Cu(II) ion; Agricultural Wastes; Isotherms.

Introduction

The release of heavy metals into our environment is still large. In certain areas of the world it is even increasing. The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. It is well known that some metals can have poisonous or otherwise toxic to human beings and ecological environments, include chromium, antimony, copper, lead, mercury, cadmium, manganese etc [1-3].

Since copper is a widely used material, there are many actual or potential sources of copper pollution. Copper may be found as contaminant in food, especially shellfish, liver, mushrooms, nuts, and chocolate. Briefly, any processing or container using copper material may contaminate the product such as food, water or drink. Copper is essential to human life and health but, like all heavy metals, is potentially toxic as well. For example, continued inhalation of copper-containing spray is linked with an increase in lung cancer among exposed workers.

There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electro dialysis [4,5]. However, these methods are not

widely used due to their high cost and low feasibility for small-scale industries [6]. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient [7]. Non-conventional materials have been tested in a large scale for this purpose, such as fly ash [8], lignite [9], tree fern [10], etc. In this paper, orange peel, sawdust and bagasse have been used as adsorbents to remove Cu(II) from aqueous solution. Orange peel, sawdust and bagasse are often considered as solid wastes of agriculture. Especially sawdust and bagasse are widely available [11,12]. These materials cause a significant disposal problem. Efforts have been made to use the cheapest and unconventional adsorbents to adsorb heavy metals such as Cu(II) ion from aqueous solution.

Experiment

Materials and Methods

Reagents: Copper(II)chloride dehydrate, sodium carbonate, potassium iodide, starch and sodium chloride were purchased from BDH; sodium thiosulfate, potassium dichromate, ammonium thicyanate, acetic acid and phosphoric acid were purchased from E. Merck (India).

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Materials

Adsorbent: Sawdust (mango tree) and bagasse were collected from local sawmill and Pabna Sugar Mills Ltd., respectively. Orange peel was collected from the local fruit juice market in Dhaka city. The collected materials were dried in the sun light for 4/5 days and crushed using a crushing mill, separately. The powdered materials were sieved using a 425 μm sieve. The powdered materials were then preserved in a number of separate containers.

Then the sawdust and bagasse powder were treated with 1 % H_3PO_4 separately. The treatment was carried as follows:

About 10g of powdered material was added to 500 mL of 1% H_3PO_4 solution. It was heated for about 20 minutes under laboratory Bunsen burner. The heated solution was kept to be cooled. Then the slurry was filtered using suction pump. The residue was washed repeatedly until freed from acid. Then the washed material was dried in the sun light for 2/3 days and crushed again. The powder materials were sieved using the same sieve (425 μm) and preserved in separate containers.

Preparation of solutions

Adsorbate solution: 2.68 g of Cu(II)chloride dihydrate was taken in a 500 mL volumetric flask and then diluted with deionized water up to the mark. The resulting concentration of the copper solution was 1000 $\mu\text{g/mL}$ (1000 ppm).

Thiosulfate solution: 0.6205 g of sodium thiosulfate was taken in a 250 mL volumetric flask and diluted up to the mark using deionized water. The concentration of the solution was 1.0×10^{-2} M. Then the solution was diluted 10 times (1.0×10^{-3} M).

Potassium dichromate solution: 14.71g of potassium dichromate (MW 294.18) was taken in a 500 mL volumetric flask and diluted up to the mark using deionized water. The concentration of the solution was 0.1 M. Then the solution was diluted 10 times (1.0×10^{-2} M).

Starch solution: 1 g of the starch was taken in a 250 mL beaker and 100 mL hot water was added with continuous stirring. The solution was then filtered and preserved in a reagent bottle.

Potassium iodide solution (10%): 50 g of the iodate free potassium iodide was taken in a 500 mL volumetric flask. The volume was then adjusted up to the mark by adding deionized water.

Ammonium thiocyanate solution: 50 g of ammonium thiocyanate was taken in a 500 mL volumetric flask. The volume was then adjusted up to the mark by adding deionized water. The resulting concentration of the ammonium thiocyanate solution was 10%.

Dilute acetic acid: Requisite volume of the glacial acetic acid was poured in a 250 mL volumetric flask. The volume was adjusted to the mark with deionized water.

Procedure

Batch adsorption experiments were carried out by shaking 1 g of each adsorbent with 100 mL of the copper solution of 100 $\mu\text{g/mL}$ concentration at room temperature. At the end of the predetermined time interval, the adsorbent was removed by centrifugation. The amount of copper in the centrifugate was analyzed iodometrically through standard addition method.

Standard addition method: 25 mL of each centrifugate was taken in a 50 mL volumetric flask and then 5 mL of 1000 $\mu\text{g/mL}$ of copper solution was added. The final volume was adjusted to the mark by addition of deionized water. The following iodometric method was used through out the experiment.

Standardization of $\text{S}_2\text{O}_3^{2-}$ solution: 50 mL deionized water was taken in a conical flask and 10 mL 10% iodate free potassium iodide and 1-2 g pure sodium bicarbonate was added with shaking to dissolve the bicarbonate. 5 mL (conc). HCl was added slowly and gently rotated. Then 10.0 mL of 0.1M standard potassium dichromate solution by a pipette mixing the solution well and washed with the sides of the flask with deionized water. Then the flask is covered and left in dark for about 5 minutes. Dilute the solution with deionized water to about 150 mL. The liberated iodine was titrated with freshly prepared $\text{S}_2\text{O}_3^{2-}$ (1.0×10^{-3} M) solution from a burette. When most of the iodine has reacted (the color of the solution became yellowish green) then 1.0 mL of the starch solution was added and the sides of flask was rinsed with deionized water. The addition of $\text{S}_2\text{O}_3^{2-}$ was continued until one changes the color to light green. The titration was repeated three times.

Iodometric method: 20 mL of the experimental copper solution was taken in a 250 mL conical flask. The solution was acidified with few drops of concentrated HCl. Then requisite amount of solid sodium carbonate was added until a bluish permanent precipitate (ppt) was observed. The ppt was dissolved by the addition of acetic acid. 10 mL of 10 % KI was added and kept in

dark for about five minutes for iodine liberation. After five minutes the solution was taken out and diluted with deionized water to about 150 mL. The flask was rinsed with deionized water. The liberated iodine was titrated with the freshly prepared $S_2O_3^{2-}$ (1.0×10^{-3} M) solution from a burette. When most of the iodine has reacted (the color of the solution became yellowish green) then 1.0 mL of the starch solution was added and the sides of the addition of $S_2O_3^{2-}$ was continued until one changes the color to light green. Then a few drops of NH_4CNS solution was added and the color was more intensified. The titration was repeated at least two times. The amount of copper was calculated from the volume of thiosulfate used. Routine standardization of the thiosulfate solution was carried by standard potassium dichromate using iodometric method [13].

Apparatus

The following apparatus were used as follows: Centrifuge machine (4000 rpm KOKUSAN, Japan), pH meter: TOA pH meter (HM 16S, Japan), Oven (NDO-450ND, EYELA, Japan) and Electrical Balance, Model ALC 110.4, ACCULAB, SWEDEN.

Results and Discussion

Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process and thus the effect of pH has been studied by varying it in the range of 2-10 as shown in Fig. 1.

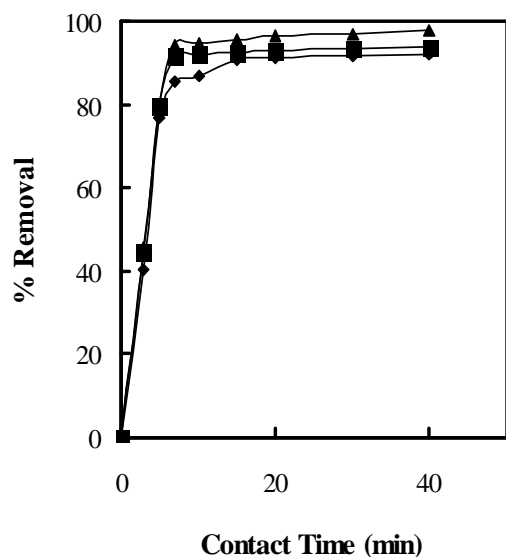


Figure 1. Effect of pH on the adsorption of copper on the non-treated and treated adsorbents. $[Cu(II)] = 100$ ppm; Contact time = 60 min; Temperature = 25 °C. ▲: orange peel; ■: raw saw dust; ◆: raw bagasse; —: treated sawdust; ●: treated bagasse

The results showed that the retention of copper by the non-treated orange peel increases while the pH increasing until a certain value, it increases between pH 2.0 and 6.2, after that the capacity of adsorption decreases slightly in pH range of 8-10. The maximum adsorption efficiency in the range of 2-8 may be due to the interaction of Cu^{2+} , $Cu(OH)^+$, $Cu(OH)_2$ with surface functional groups present in the non-treated orange peel. Decreasing in adsorption at high pH may be due to the formation of soluble hydroxy complexes [14].

At pH 6 there are three species present in solution as suggested by Elliot and Huang [15]: Cu^{2+} in very small quantity and $Cu(OH)^+$ and $Cu(OH)_2$ in large quantities. These species are adsorbed at the surface of the non-treated adsorbent by ion exchange mechanism with the functional groups present in the non-treated adsorbents or by hydrogen bonding as shown below:

- (a) Ion exchange
 $(-RO^+H_2) + Cu^{2+} \rightarrow (RO)Cu + 2H^+$
 $-RO^+H_2 + Cu(OH)^+ \rightarrow (-RO)CuOH + 2H^+$
- (b) Hydrogen bonding
 $2(-ROH) + Cu(OH)_2 \rightarrow (-ROH)_2---Cu(OH)_2$

where $-R$ represents the matrix of adsorbent.

In addition, the raw materials also contain carboxylic group containing ingredients which cause the interaction with the copper. The carboxylic groups present in the adsorbents having the pK_a values from 3 to 5. Therefore, at higher pH, deprotonation occurs, resulting more interaction between the negatively charged carboxylate and positively charged copper species.

Similar trend of copper removal was observed by the other non-treated adsorbents, such as sawdust and bagasse, with lower percentage of the removal. The lower percentage of the removal of copper may be the lower percentage of cellulosic materials present in the raw sawdust and bagasse.

Effect of contact time

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. Consequently it is important to study its effect on the capacity of retention of copper by adsorbents like orange peel, sawdust and bagasse. Figure 2 indicates the typical form of saturation curves showing that the equilibrium is attained at 7 minutes for all the adsorbents. There is no change the uptake of copper by the adsorbents after about 7 min although all the experiments were carried out up to 40 min. This is due to saturation of the adsorbents by the copper.

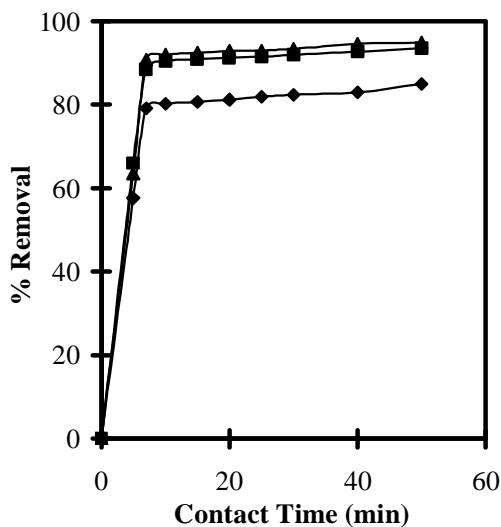


Figure 2. Effect of contact time on the adsorption of copper by the non-treated adsorbents. [Cu(II)] = 100 ppm; Amount of adsorbent = 1 g ; pH = 6.40; Temperature = 25 °C. ▲: orange peel; ■: raw saw dust; ◆: raw bagasse

Effect of the initial concentration

Figure 3 shows the effect of the initial concentration of copper on the adsorption by the adsorbents. The trend of removal of copper is irrespective of the adsorbents. High percentage of removal was observed for lower concentration of copper for all the adsorbents but the uptake of copper by unit weight of the adsorbent was the same. Figure 3(a), (b), and (c) indicate the effect of initial concentration of copper on orange peel, raw sawdust and raw bagasse, respectively.

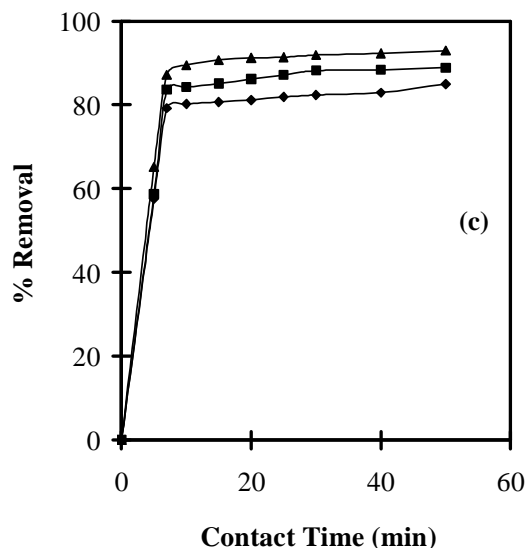
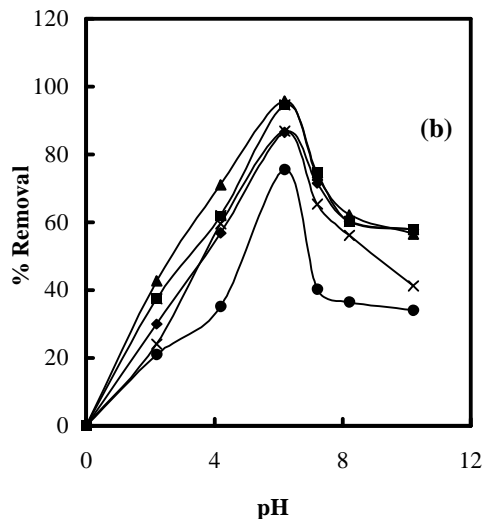
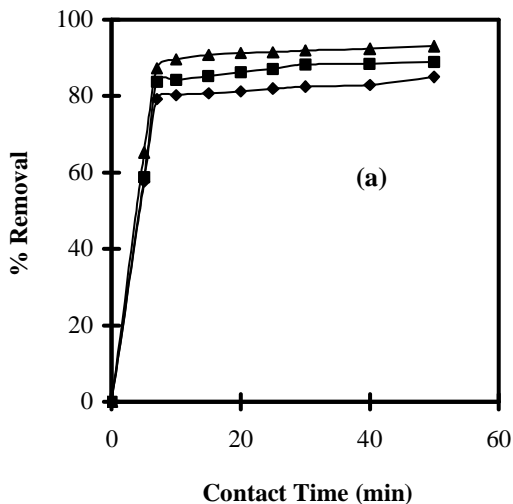


Figure 3. Effect of initial concentration on the adsorption of copper by the non-treated adsorbents. Contact Time = 50 min; Amount of adsorbent = 1g/100 mL; pH = 6.40; Temperature = 25 °C. ◆: 120; ■: 100; ▲: 80 ppm. (a): Orange Peel; (b): Raw Sawdust; (c): Raw Bagasse

Effect of adsorbent dosage

To study the influence of the liquid to solid ratio on the retention of copper, three different values have been taken by varying the adsorbent amount of the support while keeping the volume of the metal solution constant as shown in Figure 4 where it can be seen that the adsorption increases with the increase in the amount of the adsorbents. This can be explained by a greater availability of the exchangeable sites or surface area at higher amount of the adsorbent. The adsorption percentage increases from the doses of 0.25 g/100ml to 1 g/100ml rapidly. But no significant adsorption was found beyond 1g/100ml.

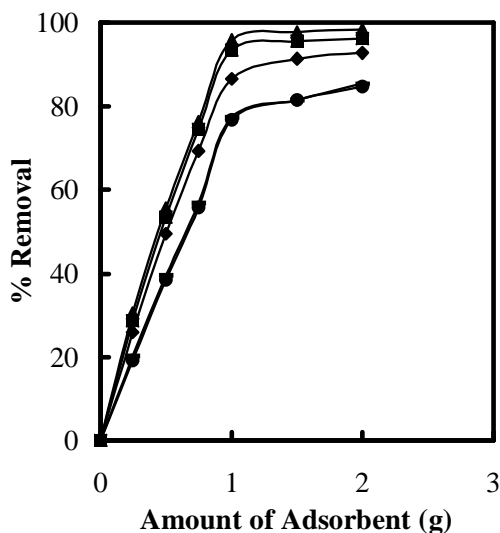


Figure 4. Effect of adsorbent dosage on the adsorption of copper
Contact Time = 50 min; Amount of adsorbent = 0.25, 0.5, 0.75, 1.0, 1.5 and 2.0 g/100mL; pH = 6.40; Temperature = 25°C. ▲: orange peel; ■: raw saw dust; ◆: raw bagasse; —: treated sawdust; ●: treated bagasse

Effect of the ionic strength

Figure 5 shows the influence of the ionic strength on the capacity of adsorption. It was tested by the addition of sodium chloride to the copper solution. The increase in ionic strength between 0.001 and 0.1 decreased the percentage of adsorption from 70.3 to 30.7, 73.7 to 32.1, 75.3 to 36.4, 53.2 to 25.7, 55.4 to 27.7 on bagasse, sawdust, orange peel, treated bagasse, treated sawdust respectively.

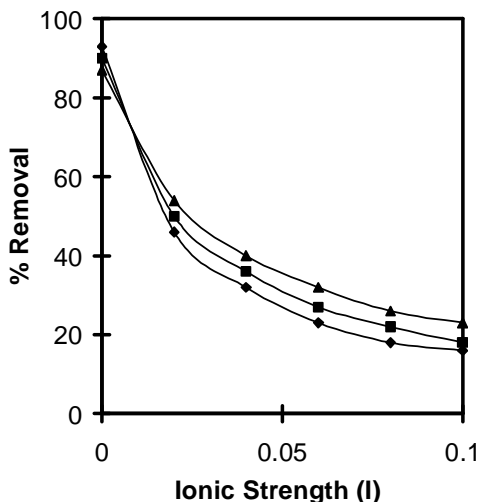


Fig 5. Effect of ionic strength on the removal of Cu (II) from aqueous solution using the raw adsorbents: ◆: orange peel; ■: sawdust; ▲: bagasse. [Cu(II)] = 100 ppm; contact time = 60 minutes; Temperature: room temperature. Amount of adsorbent=1g/100mL. pH=6.4

The ionic strength effect can be explained as follows: The electrostatic attraction seems to be a significant mechanism, as indicated by the results where at high ionic strength, the increased amount of NaCl can help to render the surface of the sawdust not easily accessible to copper (II) ions and hence decreasing the percent of removal. In fact according to surface chemistry theory developed by Gouy-Chapman [16] when solid adsorbent is in contact with adsorbate species in solution, they are bound to be surrounded by an electrical diffused double layer, the thickness of which is significantly expanded by the presence of electrolyte. Such expansion inhibits the adsorbent particles and Cu (II) from approaching.

Therefore, the ionic strength effect indicated that the adsorption of copper on the adsorbent follows ion-exchange mechanism.

Analysis of the adsorption capacity by means of the Langmuir and Freundlich models

The study of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximal capacity of adsorbents. In order to adapt for the considered system, an adequate model that can reproduce the experimental results obtained, shown in Table 1 have been considered. Generally the Langmuir equation applies to the cases of adsorption on completely homogeneous surfaces where interactions between adsorbed molecules are negligible. While the equation of Freundlich applies fairly well when describing the adsorption in aqueous systems. It can be seen that the correlation factor is close to unity for both models, indication a good representation of the experimental results by using the Langmuir isotherm as shown in Figure 6.

Table 1. Values of Langmuir Constants

Name of Adsorbents	R ²	Q (mg/g)	b (mg/L)
Orange peel	0.991	3.19	1.21
Sawdust	0.994	3.12	1.09
Bagasse	0.997	2.89	0.99

The present study thus reveals that the adsorbents such as orange peel, sawdust and bagasse are excellent adsorbents for the removal of copper from aqueous solution. The small variation in the adsorption capacity for the adsorbents is due to the presence of different percent of the constituents which are actually bind with the divalent metal ion, Cu(II). In addition, the treated sawdust showed little bit lower percent removal compared to its non-treated form. This is due to maximal removal of cellulosic materials during the acid

treatment resulting lower of binding sites of the adsorbents. The investigations are quite useful in developing a wastewater treatment plant. The process is economically feasible and easy to carry out.

References

1. L. Bartlett, F. W. Rabe and W. H. Funk, *Wat. Res.*, 8 (1974) 179.
2. T. Bednarz and H. D. Warkowska, *Acta Hydrobiol.*, 26 (1984) 389.
3. R. G. Jak, J. L. Maas and M. C. T. Scholten, *Wat. Res.* 30 (1996) 1215.
4. M. Sitting, *Handbook of Toxic and Hazardous Chemicals*, Noyes Publications, Park Ridge, NJ, 1981. J. W. Patterson, *Industrial Wastewater Treatment Technology*, 2nd ed., *Butterworth-Heinemann, London*, (1985).
5. A. Sohail, S.I. Ali, N. A. Khan and R.A.K. Rao, Removal of chromium from wastewater by adsorption, *Environ. J. Pollut. Contr.*, 2 (1999) 27.
6. S. S. Gupta and K. G. Bhattacharyya, Removal of Cd(II) from aqueous solution by kaolinite, montmorillonite and their poly(oxo-zirconium) and tetrabutylammonium derivatives, *J. Hazard. Mater. B* 128 (2006) 247.
7. A. Mathur and D.C. Rupainwar, *Asian Environ.*, 10 (1988) 19.
8. N. Balasubramanian and A. J. Ahamed, *Pollut. Res.*, 17 (1998) 341.
9. Y.S. Ho, *Water Res.*, 37 (2003) 2323.
10. W. J. Chen and X. G. Cheng, Using sulfuric acid to measure the lignin of peanut husk, *J. Minjiang University*, 23 (2) (2002) 72.
11. L. J. Yu, S. S. Shukla and K. L. Dorris, Adsorption of chromium from aqueous solutions by maple sawdust, *J. Hazard. Mater.*, 100 (2003) 53.
12. J. Mendham, R. C. Denney, J. D. Barnes, M. J. K. Thomas, R. C. Denney and M. J. K. Thomas, *Vogel's Text Book of Quantitative Chemical Analysis*, 6th ed., *Prentice, New Jersey, USA*, (2000).
13. M. Ajmal, A. H. Khan, S. Ahmad and A. Ahmad, Role of sawdust in the removal of Copper(II) from industrial wastes, *Water Res.*, 32 (1998) 3085.
14. H. A. Elliot and C. P. Huang, Adsorption characteristics of some Cu(II) complexes on aluminosilicates, *Water Res.*, 15 (1981) 849.
15. P. C. Hiemenz and R. Rajagopalan, *Principles of Colloid and Surface Chemistry*, p. 516, 3rd ed., *Marcel Dekker, New York*, (1977)

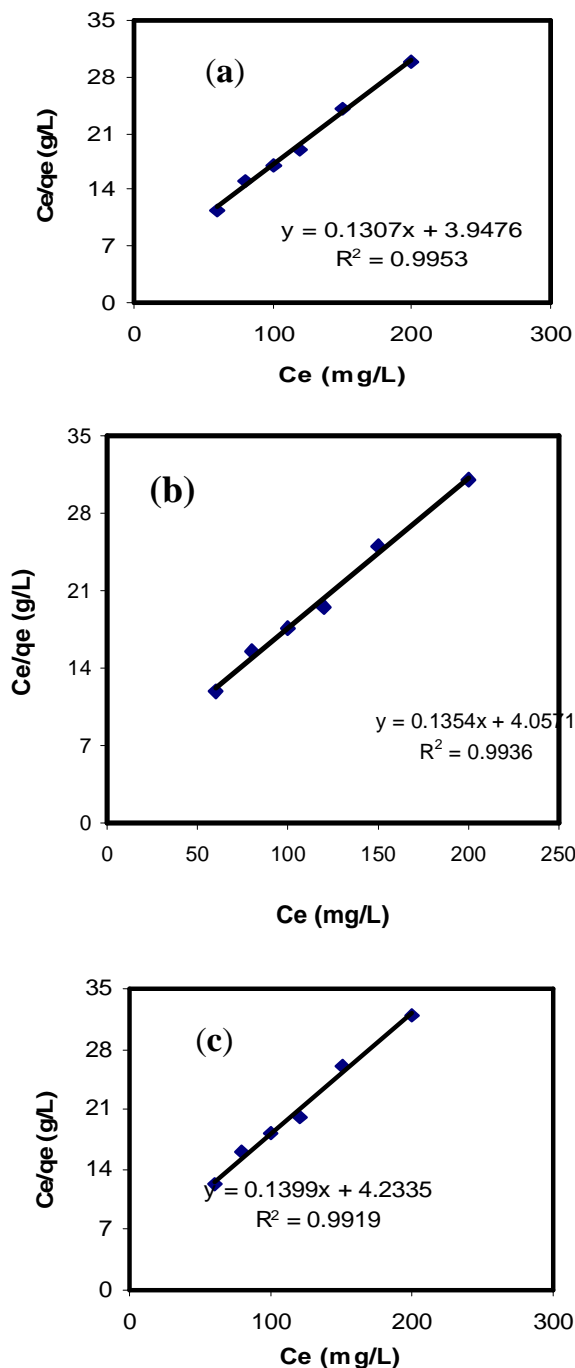


Figure 6. Adsorption isotherms for the sorption of Cu(II) ion on the adsorbents.