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Removal of Cu (II) Ions from Aqueous Solution by Carbon Prepared from Henna Leaves, Pungam Bark and CAC

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ABSTRACT

Activated carbon prepared from Henna leaves and pungam tree bark, an agricultural solid waste by-products and CAC for the removal of copper from aqueous solutions has been studied. Parameters such as equilibrium time, effect of pH and adsorbent dose on removal were studied. The adsorbent exhibited good sorption potential for copper at pH 5. The experimental data were analysed by both Freundlich and Langmuir isotherm models. The sorption kinetics of the copper have been analysed by Lagergren pseudo-first-order and pseudo-second-order kinetic models.

Key Words: Adsorption, Activated Carbon, Adsorbent, Isotherms, Kinetics.

INTRODUCTION

Heavy metal ions have become an ecotoxicological hazard of prime interest and increasing significance, because of their accumulation in living organisms [1]. Copper pollution arises from copper mining and smelting, brass manufacture, electroplating industries and excessive use of Cu-based agri-chemicals. Copper along with arsenic and mercury, is recognized as the highest relative mammalian toxic [2] and continued inhalation of copper containing sprays is linked with an increase in lung cancer among exposed workers [3]. Maximum acceptable copper concentration in drinking water is less than 3000_g/dm^3 [5,6]. Hence, removal of copper from water and wastewater assumes importance. The conventional methods for heavy metal removal from water and wastewater include oxidation, reduction, precipitation, membrane filtration, ion exchange and adsorption. Among all the methods adsorption is highly effective and economical. Though the use of commercial activated carbon is a well-known adsorbent for the removal of heavy metals from water and wastewater, the high cost of activated carbon limits its use as an adsorbent in developing countries. Hence, it is a growing need to derive the activated carbon from cheaper and locally available waste materials. Several research workers used different low-cost adsorbents from agriculture wastes such as coconut coirpith [8], sawdust [3], rice husk [9], banana pith [10], cottonseed hulls [11], apple wastes [12], sugarcane bagasse pith [13], peanut hull carbon [14], activated carbons obtained from agricultural by-products [15] and Mn-oxide coated granular activated carbon [16] for the removal of copper from water and wastewater. In spite of several researchers adopted various low-cost adsorbents there is still a need to develop suitable adsorbents for the removal of copper from aqueous solutions. Studies were carried out in the removal of copper from aqueous solutions using activated carbon derived from Henna leaves and pungam tree bark. The henna plant is native to tropical and subtropical regions of Africa, southern Asia, and northern Australasia in semi-arid zones. Pongamia plant, one of the herbs, found throughout India up to 1300 meters altitude, along the streams and river, mainly in Andhra and Madhya Pradesh, Kerala, Maharashtra and Tamil Nadu. It is an evergreen, medium-sized glabrous tree. A commercial activated carbon (CAC) of M/S. S.D. fine chem., Mumbai, India was procured from the market for the purpose of comparison. All these three carbons were powdered and a particle size of 80-120 mesh (ASTM) was considered for studies.

EXPERIMENTAL SECTION

2.1. Instrumentation

A UV spectrometer was used for determining copper concentrations. An Elico pH meter was used for pH measurements. A mechanical shaker was used for agitating the samples.

2.2. Chemicals

All the chemicals used were of analytical reagent grade. Deionised doubly distilled (DDD) water was used throughout the experimental studies. Stock copper solutions (1 mg/ml) were prepared by dissolving $CuNO_3 \cdot 5H2O$ in 1000 ml of DDD water. Working standards were prepared by progressive dilution of stock copper solutions using DDD water. ACS reagent grade HCl, NaOH and buffer solutions were used to adjust the solution pH.

2.3. Procedure of adsorbent preparation and activation

Henna leaves and Pungam tree bark were collected from local fields and cut to a small pieces, washed several times with DDD water and left to dry. The carbonisation of leaves and bark were performed by adding sulphuric acid and washed with double deionised water. Finally, the material was sieved to 120-mesh size and stored in desiccator for further use.

2.4. Adsorption studies

Batch adsorption experiments were carried out in a series of stoppered reagent bottles. A weighed amount (0.5 g) of adsorbent was introduced into reagent bottles (100 ml) containing various concentrations with 50 ml aqueous solutions of copper. The solution pH was adjusted to the desired value by adding HCl or NaOH. Then, the bottles were shaken at room temperature ($30\pm1^{\circ}C$) using a mechanical shaker for a prescribed time to attain the equilibrium. The solutions were filtered and the concentrations of metal ions were determined by UV visible spectrometer. The effects of concentration (50–100 mg/l), contact time (10–120 min), solution pH (1.5-6 for Cu), temperature (30-60) and adsorption dose (0.3–0.7 g) were studied. Blank solutions were treated similarly (without adsorbent) and the recorded concentration by the end of each operation was taken as the initial one.

RESULTS AND DISCUSSION

Effect of contact time

Figure 1 (a) indicate the effect of contact time on removal of cation ions Cu (II). The effect of contact time was studied in the range of 10, 20, 30, 40, 50, 60, 90 and 120 min. It was found that equilibrium time to remove these metal ions was 60 min. The results showed that the removal percentage order at equilibrium was CAC > HLC > PBC. These results are important, as equilibrium time is one of the important parameters in adsorption, when the time consumed for industrial wastewater disposal should be considered (Esposito *et al*, 2002).

Effect of initial metal ion concentration

The effect of initial metal ion concentration on percentage metal removal is also shown in Figure 1 (b). The concentrations in the range from 50 ppm to 100 ppm for the metal ions have been studied. The removal of metal ions by Pungam bark , Henna leaves and CAC were found to increase with increase in initial metal concentration. This was due to the increase of metal ions concentration which was completed on the effective site as this may be a limited active site for adsorbent material. Therefore, more metal ions were left unabsorbed in solution at higher concentration levels. (Asubiojo and Ajelabi, 2000).

Effect of pH

Effect of pH on process of adsorption movement on Pungam bark and Henna leaves were studied in the range from 1 to 6 (Figure1(c)). It was noticed that the ability of removing copper by adsorbent depends on pH of solution and this depends on the ion state and nature of material. In low pH value, binding sites are generally protonated or positively charged (by the hydronium ions). Thus, repulsion occurs between the metal cation and the adsorbent at a higher pH value; binding sites start deprotonating, and makes different functional groups available for metal binding. In general, cation binding increases as pH increases (Forsner and Wittman, 1981). The experiments were carried out at different pH shows that there was a change in the quantity of adsorbed copper ions on the solid phase of Pungam bark and Henna leaves over the entire pH range from 1 to 6. This indicates the strong force of interaction between the copper ions and the Pungam bark and Henna leaves that, H+ ion could influence the adsorption capacity. Here the interaction is more at pH 5 due to the competence of acidic H+ ion with metal cation for the sorption sites (Forsner and Wittman, 1981).

Effect of adsorbent dosage:
The effect of adsorbent dosage of Pungam bark and Henna leaves with an initial concentration of 100 ppm taking the range from 0.3 g to 0.7 g was studied. It was noticed that the mass of the adsorbent material increases the ability of removal as in Figure 1(d) which represented the amount of the adsorbent at saturation stage, and also depends on the physical properties of the Pungam bark and Henna leaves. Also, from Figure 1(d), it can easily be inferred that the percent removal of metal ions increases with the increasing quantity of Pungam bark and Henna leaves. This is due to the greater availability of the exchangeable sitesor surface area at higher dose of the adsorbents. These results are in agreement with previous studies on many other adsorbents (Forsner and Wittman, 1981).

Adsorption Isotherms:
Among various plots employed for analyzing the nature of adsorbate –adsorbent interaction, adsorption isotherm is the most significant. The results of adsorption studies of Cu (II) at different concentrations ranging from 50 to 100 ppm on a fixed amount of adsorbent are expressed by two of the most popular isotherm theories viz., Freundlich and Langmuir isotherms.

Freundlich equation is given by

$q = Kf\ Ce^{1/n}$

$\ln q = \ln Kf + 1/n \ln Ce$

Langmuir equation is given by

$q = qmax\ b\ Ce/ 1+ b\ Ce$

$1/q = 1/qmax\ b\ Ce + 1/qmax.$

In the above equations, Kf and n are Freundlich constants, which affect the adsorption process, such as adsorption capacity and intensity of adsorption, respectively. The values of these constants, obtained by least squares fitting of the data on ln q and ln Ce (Figures 2 (a) and 2 (b)) are tabulated in Table 1.qmax (mgg-1) and b are Langmuir constants related to monolayer adsorption capacity and energy of adsorption respectively. The values of the parameters, evaluated by the least square fitting of the data on 1/Ce versus 1/q ..

The equilibrium of sorption is one of the important physicochemical aspects for the evaluation of the sorption process as a unit operation. The sorption isotherm studies are conducted by varying the initial concentration of copper(II) from 50 to 100 mg/L and maintaining the adsorbent dosage of 700 mg/100 mL. The adsorption isotherm (q_e versus C_e) shows the equilibrium between the concentration of copper(II) in the aqueous solution and its concentration on the solid (mass of copper(II) per unit mass of adsorbents). It is evident that adsorption capacity increases with increasing equilibrium copper(II) concentrations. Figures 2(a,b,c&d) show that the adsorption capacity increases rapidly from 0 to 5.0 mg/g for the equilibrium concentration of 0 to 35 mg/L. Further a gradual increase in adsorption capacity is observed with the increase in equilibrium concentration. In order to model the sorption behaviour, adsorption isotherms have been studied. The adsorption process of copper(II) is tested with Langmuir and Freundlich isotherm models..

The high value of correlation coefficient (R^2 = 0.999) indicated a good agreement between the parameters. The constant q_m, which is a measure of the adsorption capacity to form a monolayer, can be as high as 3.66 mg/g at pH 5 for HLC. The constant b, which denotes adsorption energy, is equal to 0.39 L/mg for HLC. The value of correlation coefficient (R^2 = 0.999) showed that the data also conform well to the Freundlich equation and the strength of the relationship between parameters is as good as in the case of the Langmuir equation.

Adsorption Kinetics:
Equilibrium study is important in determining the efficacy of adsorption. It is also necessary to identify the adsorption mechanism for a given system.Kinetic models have been exploited to test the experimental data and to find the mechanism of adsorption and its potential rate-controlling step that include mass transport and chemical reaction. In addition, information on the kinetics of metal uptake is required to select the optimum conditions for full scale batch

or continuous metal removal processes. Adsorption kinetics is expressed as the solute removal rate that controls the residence time of the sorbate in the solid–solution interface. Several kinetic models are used to explain the mechanism of adsorption processes. These models include Pseudo-first-order rate model and Pseudo-second order rate model (Rangaraj, 2003). For the data obtained in the present study, pseudofirst- order and pseudo-second-order kinetic rate models based on change in adsorbate concentration (Ce) with time are also tested (Levenspiel, 1999). Figures 3(a) & 3(b) and tabular column 2 shows the kinetic study of the adsorbents.

1(a) Effect of Contact Time

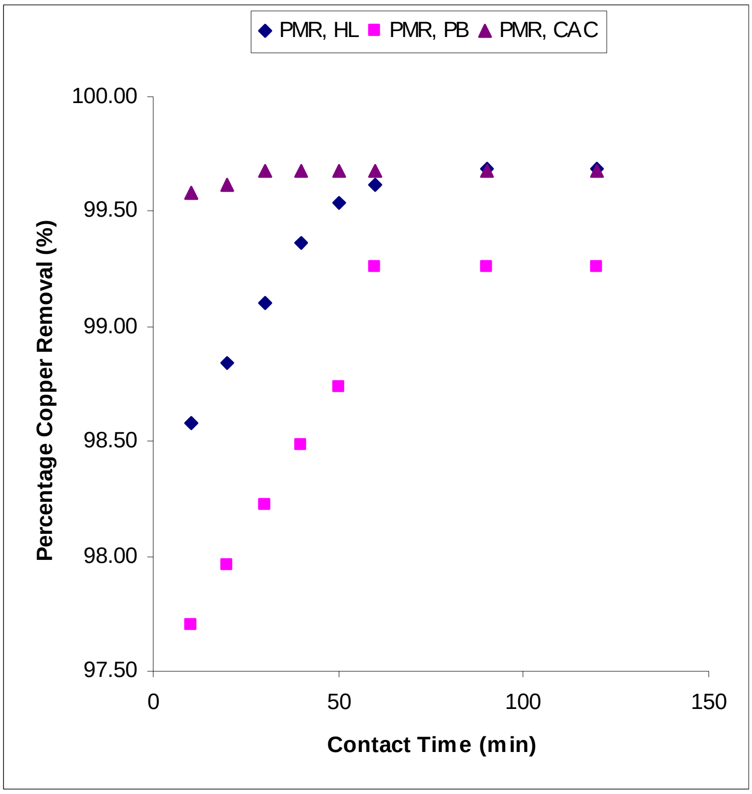


Figure 1(a). Effect of contact time on copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

1(b) Effect of initial copper concentration

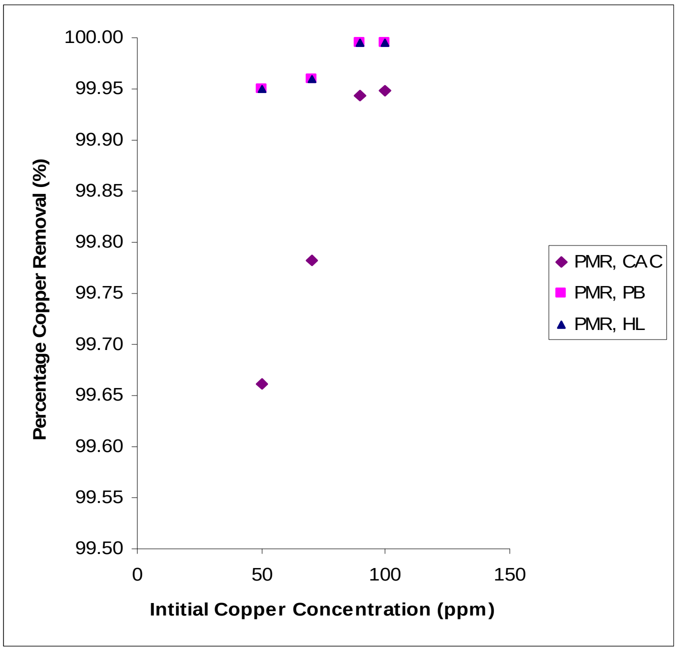


Figure 1(b) Effect of initial copper concentration on metal adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

1(c) Effect of pH

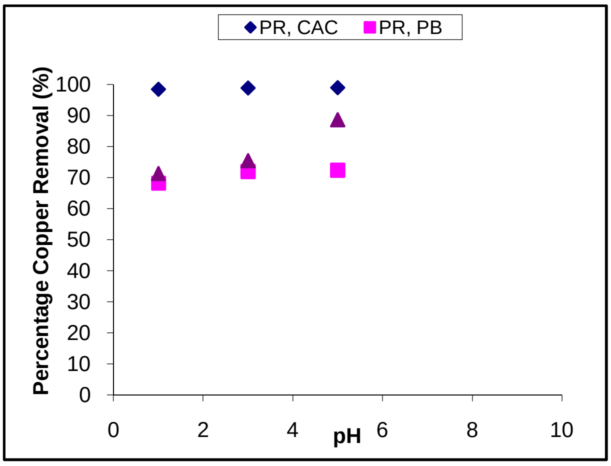
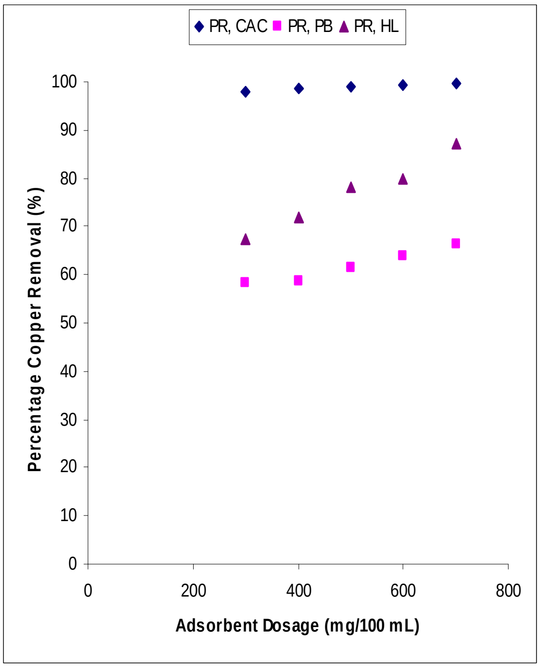


Figure 1(c). Effect of pH on copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

1(d) Effect of adsorbent dosage



1(d) Effect of adsorbent dosage on copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

1(e) Effect of temperature

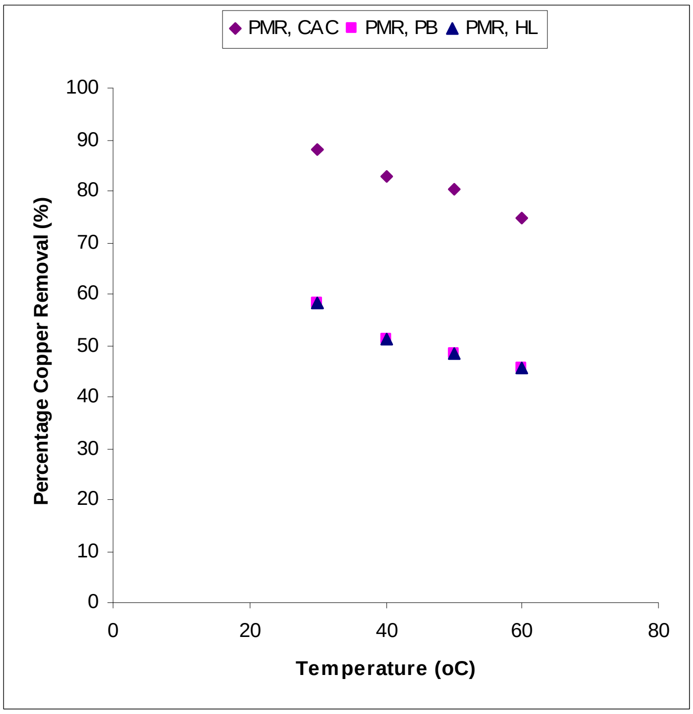


Figure 1(e) Effect of temperature on copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

2. Adsorption Isotherms

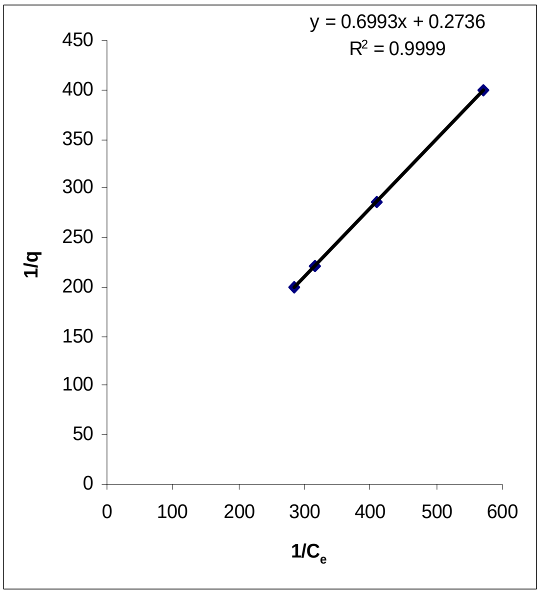


Figure 2(a) Langmuir isotherm for copper adsorption on henna leaves carbon

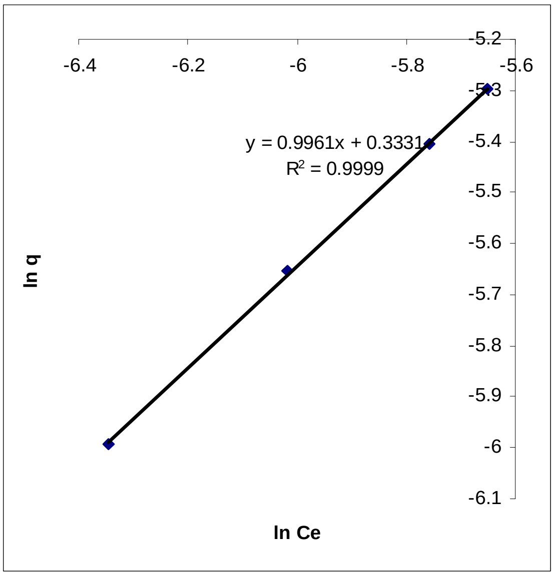


Figure 2(b) Freundlich isotherm for copper adsorption on henna leaves carbon

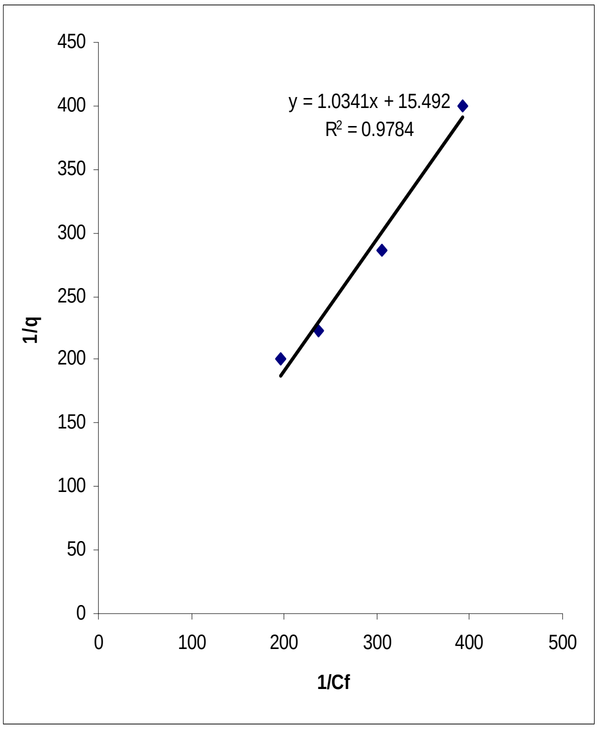


Figure 2(c) Langmuir isotherm for copper adsorption on pongamia bark carbon

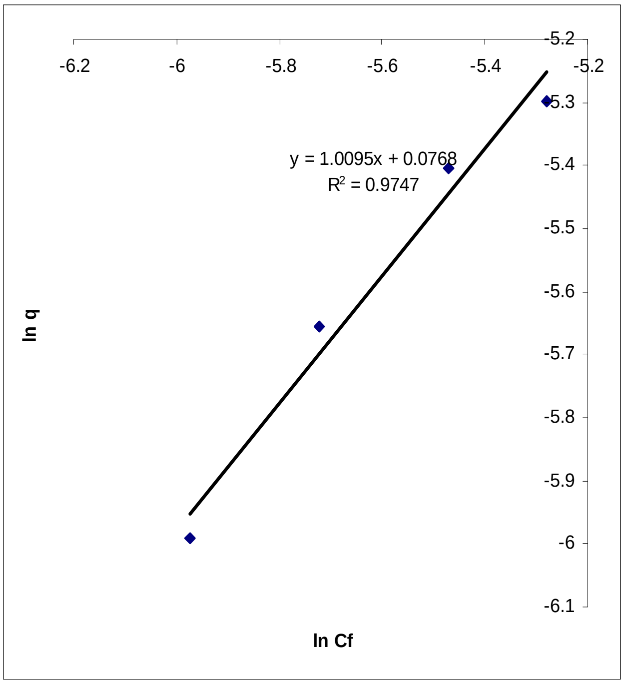


Figure 2(d) Freundlich isotherm for copper adsorption on pongamia bark carbon

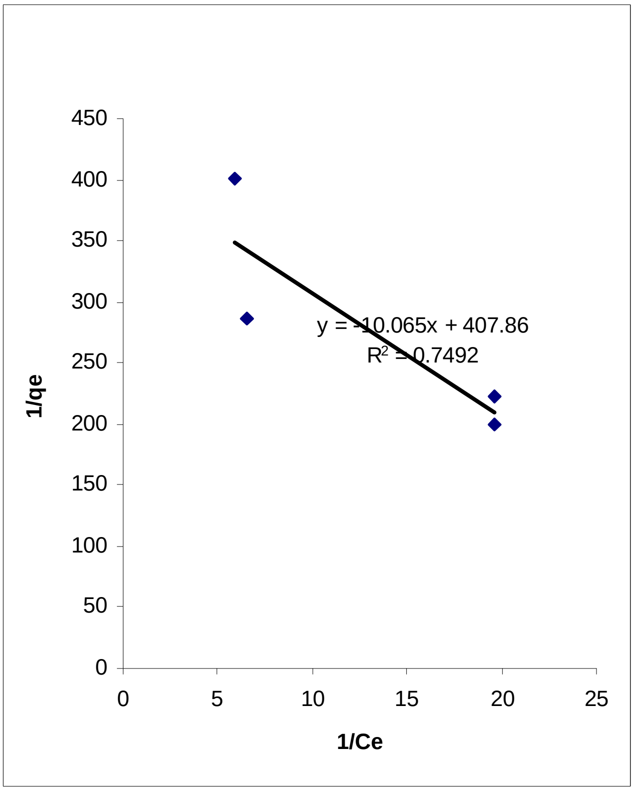


Figure 2(e) Langmuir isotherm for copper adsorption on CAC

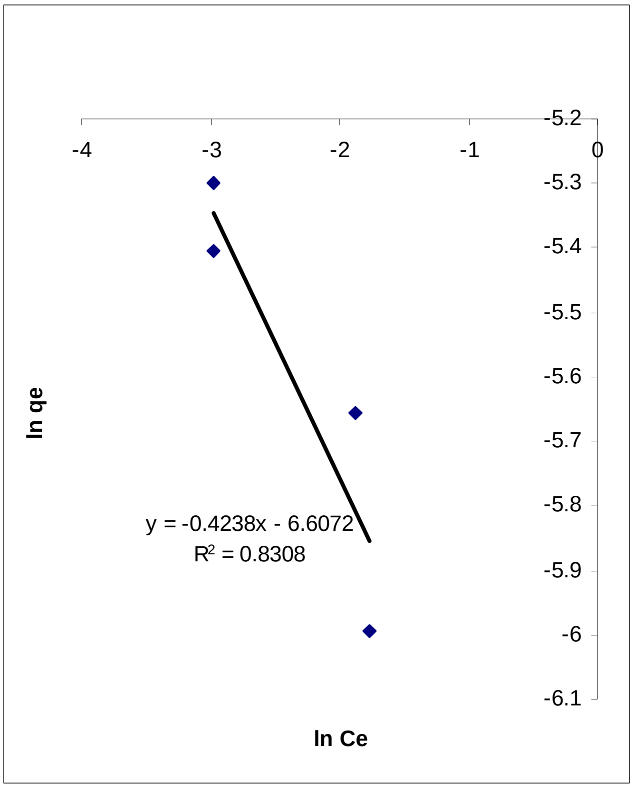


Figure 2(f) Freundlich isotherm for copper adsorption on CAC

3. Adsorption Kinetics

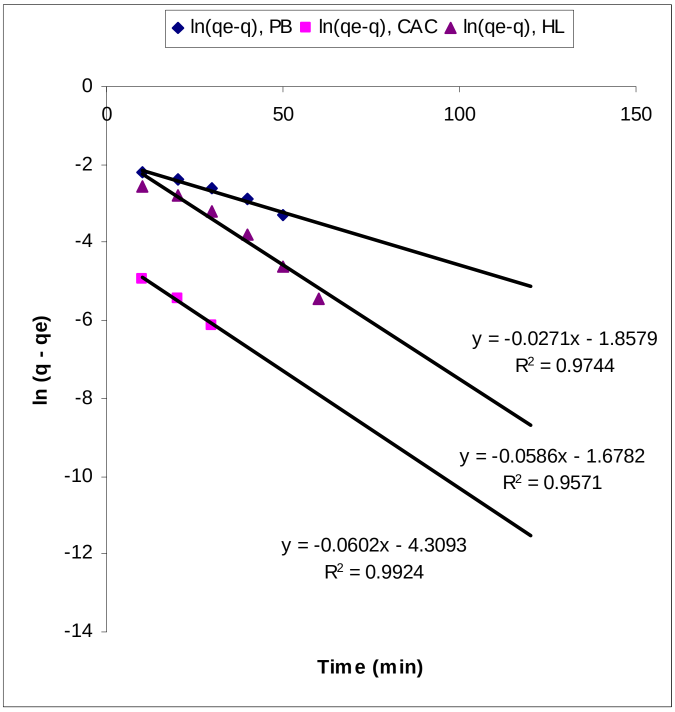


Figure 3(a) Pseudo-first order kinetics for copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

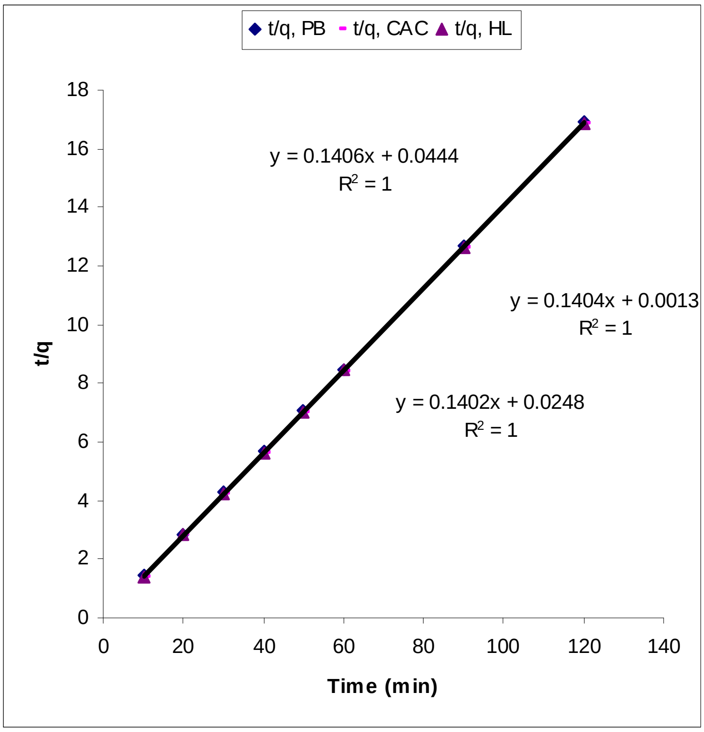


Figure 3(b) Pseudo-second order kinetics for copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

Table 1 Adsorption isotherm constants for copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

S. No.	Metal	Adsor-bent	Langmuir Isotherm			Freundlich Isotherm		
			q_{max} (mg/g)	b (L/mg)	R^2	k	n	R^2
1	Cu	HL	3.66	0.39	0.999	1.40	1.00	0.999
2		PB	0.07	15.98	0.978	1.08	0.99	0.975
3		CAC	0.01	13.02	0.866	0.01	2.10	0.828

Table 2 Adsorption kinetic constants for copper adsorption on three adsorbents (HL – Henna Leaves carbon, PB – Pongamia Bark carbon, CAC – Commercial Activated Carbon)

S. No.	Metal	Adsorbent	Pseudo First Order Equation			Pseudo Second Order Equation		
			k_1 (1/min)	q_e (mg/g)	R^2	k_2 (g/mg.s)	q_e (mg/g)	R^2
1	Cu	HL	0.027	0.156	0.974	0.793	7.133	0.999
2		PB	0.059	0.187	0.957	0.445	7.112	0.999
3		CAC	0.060	0.013	0.992	15.163	7.123	0.999

CONCLUSION

The result of batch adsorption clarifies the percentage of removal of metal ions from their wastewater solution. The initial concentration of metal ions vary from 50 ppm to 100 ppm with experimental conditions as time of contact, pH, initial concentration and the weight of loading material. The batch adsorption result showed that removal percentage was higher for Henna. Also, carbon prepared from Henna leaves and Pungam bark were found to be a promising adsorbents for the removal of metal cations from mixed metal ions solution, representing an effective and clean environment.

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