RESULTS AND DISCUSSION

4.0 RESULTS AND DISCUSSION

Environmental pollution is becoming a global problem which is an important issue as water is used directly for various purposes. The major sources of water pollution are industrial effluents and the wastewater generated from various industries, are discharged to the common drainage. The effluents pollute not only the nearby water resources but also contaminate the nearby soil and pass to other drinking water resources and hence may cause pollution of drinking water (Lokhande and Vaidya, 2004).

Rapid growth of industries and urbanization with new technical advancements have contaminated the existing water resources by discharging wastewater containing organics, colours, heavy metals from electroplating industry, mining operations and the refining of metals (Kumar, 2006). Industrial pollution is mainly caused by the discharge of industrial effluents into the water body (Rana, 2005).

Many physico-chemical methods have been proposed for their removal from industrial effluents (Iqbal *et al.,* 2002). Adsorption plays an increasingly important role in the removal of specific target compounds and a wide spectrum of compounds from water and waste water (Rathi and Puranik, 2002). Adsorption is an effective purification and separation technique used in industry especially in water and waste water treatments. Adsorption is the exchange of material at the interface between immiscible phases in contact with one another. This process is being mostly employed for the removal of dissolved substances from water and waste water (Kannan and Vanangamudi, 1991).

Some of the low cost adsorbents used to remove heavy metals are coal fly ash (Gupta and Singh, 2004), fly ash (Cho *et al.,* 2005) and agricultural waste materials like pea nut hull (Johnson *et al.,* 2002; Zacardia, 2002), bagasse (Rao *et al.,* 2003; Mohan and Singh, 2002; Khan *et al.,* 2004; Gupta *et al.,* 1999; Garg *et al.,* 2007), hazel nut shell (Cimino *et al.,* 2000), jack fruit, soy bean hull (Babel and Kurniawan, 2003), eucalyptus bark (Sarin and Pant, 2005), jack fruit peel (Inbaraj and Sulochana, 2004), rice husk (Chuah *et al.,* 2005; Khan *et al.,* 2004), olive mill residues (Veglio *et al.,* 2003), papaya wood (Saeed *et al.,* 2005), groundnut shell and saw dust (Shukla and Pai, 2005), tires and saw dust (Hamadi *et al.,* 2001), peanut husks, cassava waste (Harsfall and Abia, 2003), sago waste (Quek *et al.,* 1998), coconut tree saw dust, maize, cob, banana pith, silk (Khan *et al.,* 2004), cotton hull (Kadirvelu *et al.,* 2003), orange waste (Dhakal *et al.,* 2005; Satpute *et al.,* 2005), oil palm shell (Guo and Lua, 2002; Nomambhay and Palanisamy, 2005), tea waste (Mahvi *et al.,* 2005), corn cobs, corn strarch, pine bark (Zacardia, 2002) and modified peat resin particles (Sun *et al.,* 2004).

The present study was attempted to remove copper from synthetic metal solutions using selected agrowastes namely,orange peel, rice husk and sugarcane baggase as adsorbents, due to their easy availability.

4.1 CHARACTERISTICS OF THE SELECTED AGROWASTES

The characterization of orange peel, rice husk and sugarcane bagasse such as ash content, moisture content, bulk density, matter soluble in water and matter soluble in HCl were done. The results are shown in table 1.

In the present study Orange peel contained 7.5%, ash content, 5.25% moisture content, 0.5g/ml bulk density, 0.61% matter soluble in water and 0.8% matter soluble in HCl. Rice husk contained 9.6% ash content, 5.5% moisture content, 0.49 g/ml bulk density, 0.08% matter soluble in water and

0.38% matter soluble in HCl. Sugarcane bagasse contained 11.5% ash content, 3.5% moisture content, 0.23 g/ml bulk density, 0.21% matter soluble in water and 0.58% matter soluble in HCl.

TABLE 1

CHARACTERISTICS OF THE SELECTED AGROWASTES (ORANGE PEEL, RICE HUSK AND SUGARCANE BAGASSE)

Materials	Ash content (%)	Moisture content (%)	Bulk density (g/ml)	Matter soluble in water (%)	Matter soluble in HCl (%)
Orange peel	7.5	5.25	0.5	0.61	0.8
Rice husk	9.6	5.5	0.49	0.08	0.38
Sugarcane bagasse	11.5	3.5	0.23	0.21	0.58

Pehlivan and Cetin (2008) reported values of ash content 1.6%, moisture content 10.9%, bulk density 0.11g/ml, matter soluble in water is 0.95% and solubility in HCl is 1.14% for activated carbon.

Dhanakumar *et al.* (2007) reported that cooked tea waste contained 9.46% moisture content, 0.29% bulk density, and 5.3% water soluble compounds.

Ramakrishnan and Nagarajan (2008) reported that flame tree waste contained moisture content 8%, water soluble matter 1.1% and acid soluble matter 4.2%.

Madhavakrishnan *et al.* (2008) reported that *Ricinus communis* pericarp activated carbon contained 6.5% ash content, 2.5% moisture content, 0.46gm/l bulk density, 1.29% water soluble matter and 2.455% HCl soluble matter.

4.2 ADSORPTION OF COPPER FROM SYNTHETIC COPPER SOLUTION USING THE SELECTED POWDERED AGROWASTES

4.2.1 Effect of pH on copper adsorption

The effect of pH on the adsorption of copper from the synthetic solution is shown in Table 2 and Figure 1.

The adsorption of copper from synthetic copper solution was found to be maximum at pH 5 (75%, 73% and 81%respectively) and minimum at pH 2 (53%, 50% and 64% respectively) using orange peel, rice husk, sugar cane bagasse.

TABLE 2

MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT pH

pH	Copper levels (mg/100ml)		
	Orange peel	**Rice husk**	**Sugarcane bagasse**
2	47 (53)	50 (50)	36 (64)
3	35 (65)	45 (55)	29 (71)
4	29 (71)	32 (68)	23 (77)
5	25 (75)	27 (73)	19 (81)

The values in parentheses denote percentage adsorption of copper

Initial level of copper in the synthetic solution: 100mg/100ml

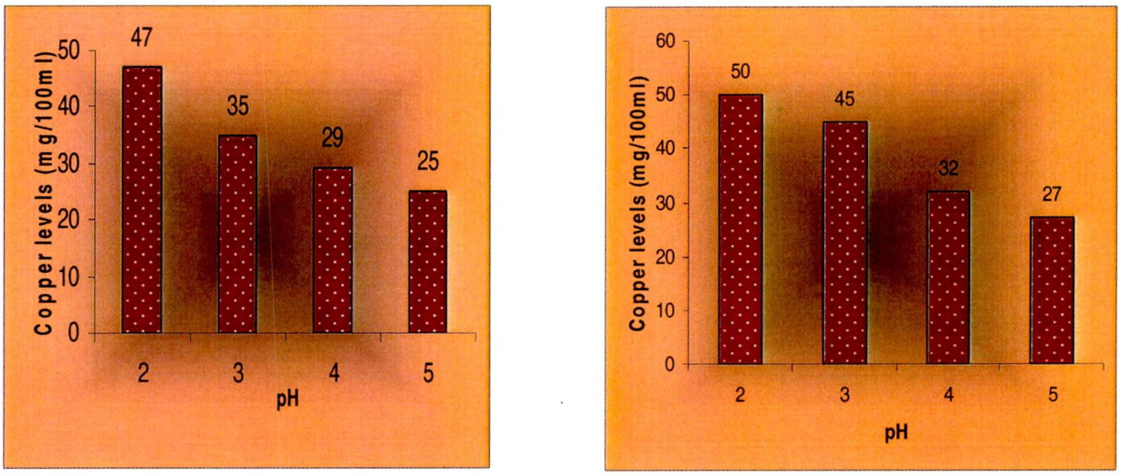
Experimental condition

Dosage of adsorbent: 1g

Temperature: Room Temperature

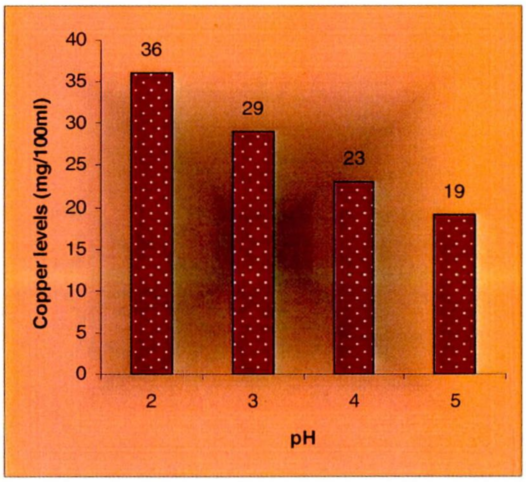
Contact time: 4 hours

FIGURE 1
MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT pH


Orange peel

Rice husk

Sugarcane bagasse



Low *et al.* (2004) reported that copper removal by the citric acid modified wood increased with pH values 2.10 – 6.15.

Verbych *et al.* (2005) reported that the chitosan removed maximum copper at pH 7.

Lee *et al.* (1999) reported that copper removal by apple residue increased from pH 5.5 to pH 7.5. There was a decrease in copper removal capacity at pH>7.5.

4.2.2 Effect of temperature on copper adsorption

The effect of temperature on the adsorption of copper from the synthetic solution is shown in Table 3 and Figure 2.

Adsorption of copper from the synthetic copper solution was found to be maximum at 30°C (72.55% and 66.67%) for orange peel and sugarcane bagssse. For rice husk the maximum adsorption occurred at the temperature 35°C (61.76%).

TABLE 3

MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT TEMPERATURES

Temperature (^{0}C)	**Copper levels (mg/100ml)**		
	Orange peel	**Rice husk**	**Sugarcane bagasse**
20	41.18 (58.82)	55.88 (44.12)	57.34 (42.66)
25	33.33 (66.67)	45.10 (54.90)	43.14 (56.86)
30	27.45 (72.55)	42.16 (57.84)	33.33 (66.69)
35	31.37 (68.63)	38.24 (61.76)	39.22 (60.78)
40	35.29 (60.71)	49.02 (50.98)	41.18 (58.82)

The values in parentheses denote percentage adsorption of copper

Initial level of copper in the synthetic solution: 100mg/100ml

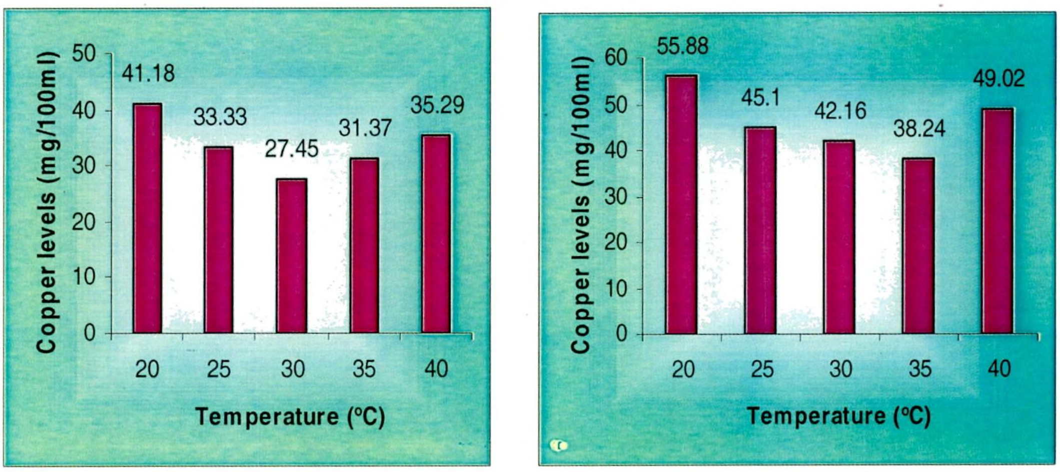
Experimental condition

Dosage of adsorbent: 1g

pH: 5

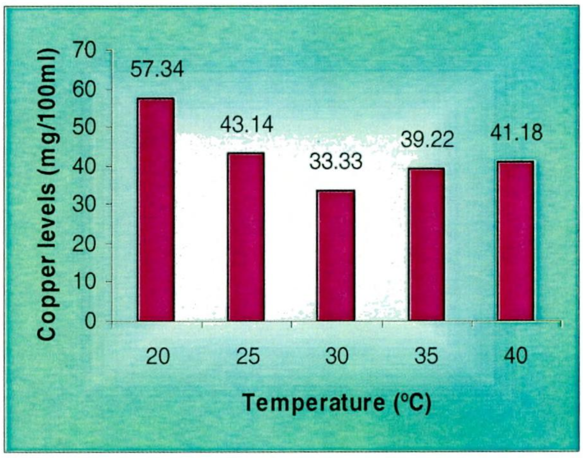
Contact time: 4 hours

FIGURE 2
MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT TEMPERATURES


Orange peel

Rice husk

Sugarcane bagasse



Antunes *et al.* (2003) reported that the capacity of copper adsorption on brown sea weed increased with increasing temperature in the range 298-329K.

Ghazy *et al.* (2004) reported that the percentage removal of copper increased as the temperature increased.

Al- Asheh *et al.* (2007) reported that the adsorption of copper by Al-Madra clay increased with a temperature range 5-50°C.

4.2.3 Effect of adsorbent dosage on copper adsorption

The effect of adsorbent dosage on the adsorption of copper from the synthetic copper solution is shown in Table 4 and Figure 3.

The copper uptake was found to increase with the adsorbents dosages. Maximum adsorption was observed with 2.5 g of orange peel, rice husk and sugarcane bagasse.

TABLE 4

MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT ADSORBENT DOSAGES

Dosage (g)	Copper levels (mg/100ml)		
	Orange peel	**Rice husk**	**Sugarcane bagasse**
0.5	49.51 (50.49)	41.75 (58.25)	48.54 (51.46)
1.0	43.63 (56.31)	37.86 (62.14)	30.10 (69.90)
1.5	37.86 (62.14)	31.07 (68.93)	27.18 (72.82)
2.0	35.92 (64.08)	27.18 (72.82)	26.21 (73.79)
2.5	30.10 (69.90)	24.27 (75.73)	21.35 (78.65)

The values in parentheses denote percentage adsorption of copper

Initial level of copper in the synthetic solution: 100mg/100ml

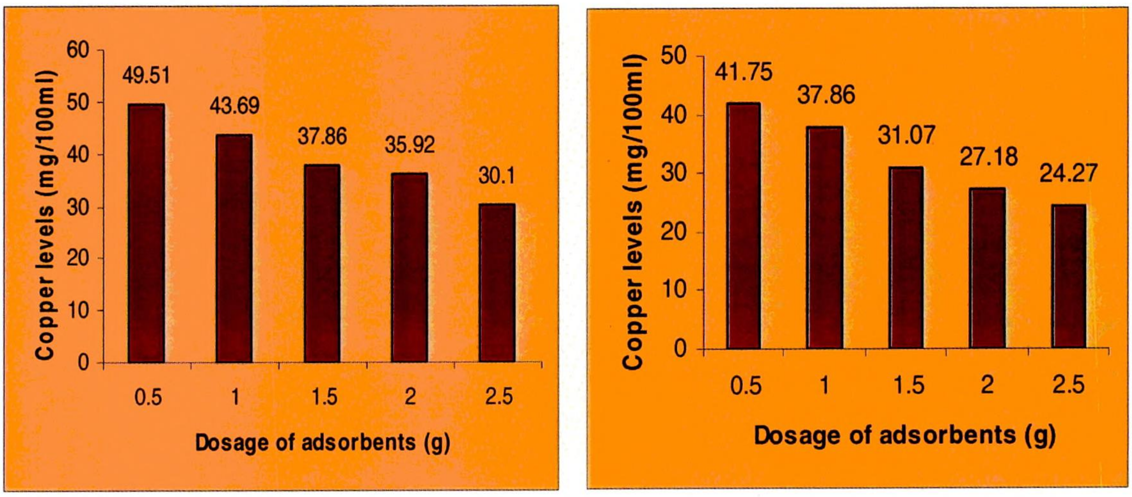
Experimental condition

pH: 5

Temperature: Room Temperature

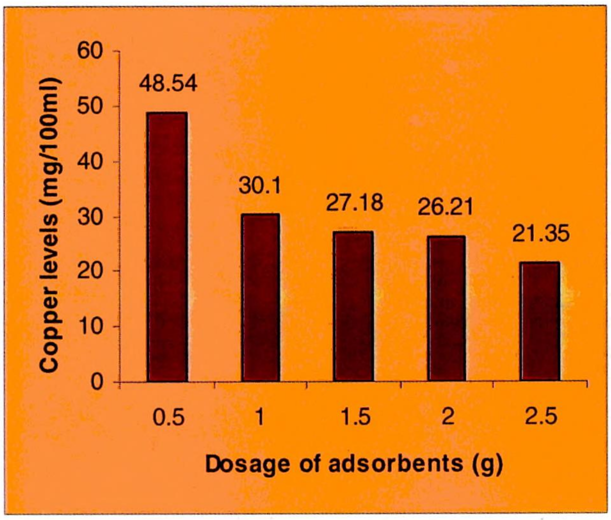
Contact time: 4 hours

FIGURE 3
MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT ADSORBENT DOSAGES


Orange peel

Rice husk

Sugarcane bagasse



Chirenje *et al.* (2005) reported that percentage metal immobilization increased significantly with increase in the amount of ash added.

Tumin *et al.* (2008) reported that the amount of copper uptake increased from 0.86 mg/g with 0.5g adsorbent up to 1.08 mg/g with 1.0g adsorbent because of the availability of exchangeable sites on the adsorbent. The copper adsorption capacity was found to decrease gradually at adsorbent dosage 2.0g with 0.41mg/g adsorption capacity and at 2.5g with 0.34 mg/g. These results may due to the clumping of adsorption particles.

Maheswari *et al.* (2007) reported that the complete removal of copper (II) from 50 ml of 25 and 50 mg/l required a maximum sago waste dosage of 175 and 225mg respectively. The increase in the percent removal of copper (II) with an increase in dosage of carbon might be due to the availability of larger surface area with more active functional groups at higher adsorbent dosage and could be suggested that saturation occurs as a result of non- availability of active sites on the adsorbent.

Gong *et al.* (2008) reported that when the wheat straw sorbent dosage was introduced from 0.5 to 2.0 g/l, the percentage of copper removal increased from 40.63% to 96.84%. With more than 2.0 g/l of sorbent dose, the equilibrium of copper removal was reached and the ratio of copper removal remained stable.

However, in the present study an equilibrium state could not be observed with the different dosage of adsorbents studied.

4.2.4 Effect of contact time on copper adsorption

Contact time is inevitably a fundamental parameter in all transfer phenomena such as adsorption. The effect of contact time on the adsorption of copper from the synthetic solution is shown in Table 5 and Figure 4.

The copper uptake was found to increase with increase in the time of contact. Maximum copper adsorption occurred at a contact time of 35 minutes and the adsorption was 60.40%, 54.46% and 58.82% for orange peel, rice husk and sugarcane bagasse respectively.

TABLE 5

MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT CONTACT TIME

Contact time (min)	Copper levels (mg/100ml)		
	Orange peel	**Rice husk**	**Sugarcane bagasse**
15	69.31 (30.69)	67.33 (32.67)	72.28 (42.16)
20	60.40 (39.60)	62.38 (37.62)	63.37 (56.86)
25	56.44 (43.56)	51.49 (48.51)	54.46 (66.67)
30	47.53 (52.47)	49.51 (50.49)	43.56 (60.78)
35	39.60 (60.40)	45.54 (54.46)	55.64 (58.82)

The values in parentheses denote percentage adsorption of copper

Initial level of copper in the synthetic solution: 100mg/100ml

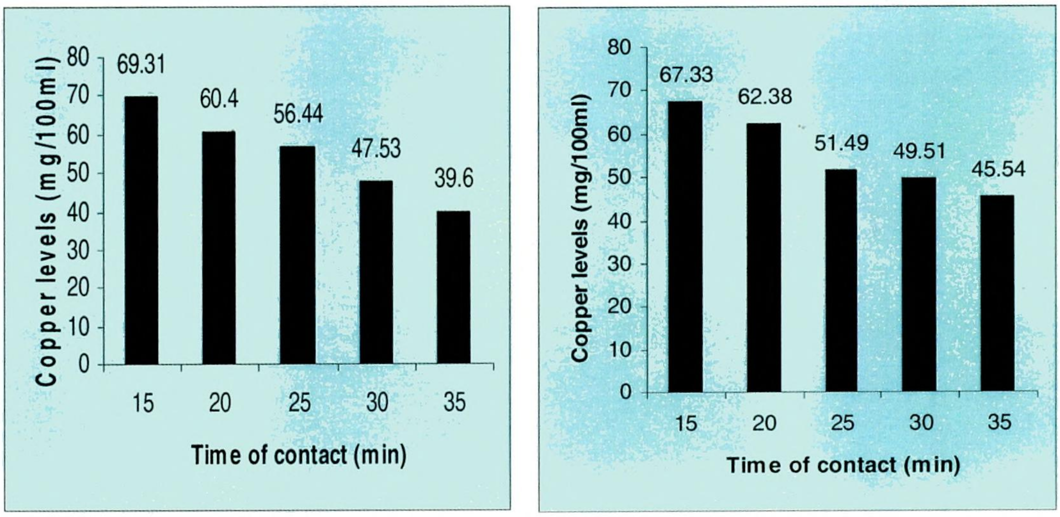
Experimental condition

pH: 5

Dosage of adsorbent: 1g

Temperature: Room Temperature

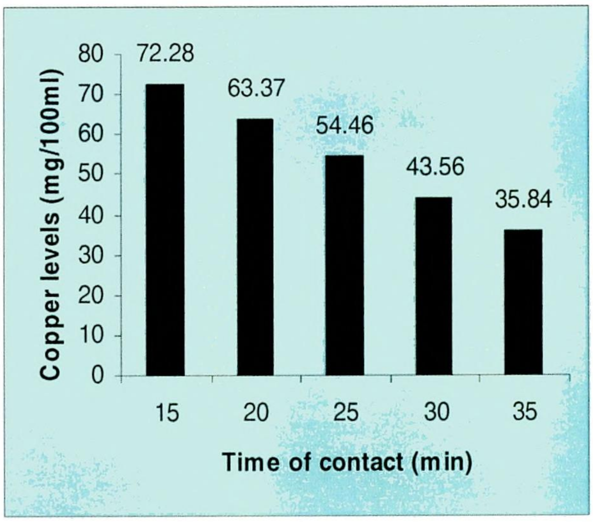
FIGURE 4
MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT CONTACT TIME



Orange peel

Rice husk

Sugarcane bagasse



Rao *et al.* (2007) reported that the sawdust adsorption capacity increased with contact time and reached equilibrium at 150 minutes for copper adsorption.

Badmus *et al.* (2006b) reported that the periwinkle shell adsorption rate was rapid within the first 120 minutes, sharply increased for 30 minutes, slowed down between 150-180 minutes and then gradually approached equilibrium after 180 minutes.

Habib *et al.* (2007) reported that the copper adsorption by sawdust attained equilibrium at 7 minutes.

4.2.5 Effect of initial concentration of copper on copper adsorption

The effect of initial concentration of copper on the adsorption of copper from the synthetic solution is shown in Table 6 and Figure 5.

The initial concentrations of copper in synthetic metal solution were 20mg/100ml, 40mg/100ml, 60mg/100ml, 80mg/100ml and 100mg/100ml.

In the present study, adsorption of copper from synthetic solution was found to be maximum at 40mg/100ml (75.95%), 60mg/100ml (74.42%), 20mg/100ml (64.5%) concentrations for orange peel, rice husk, sugarcane bagasse respectively

TABLE 6

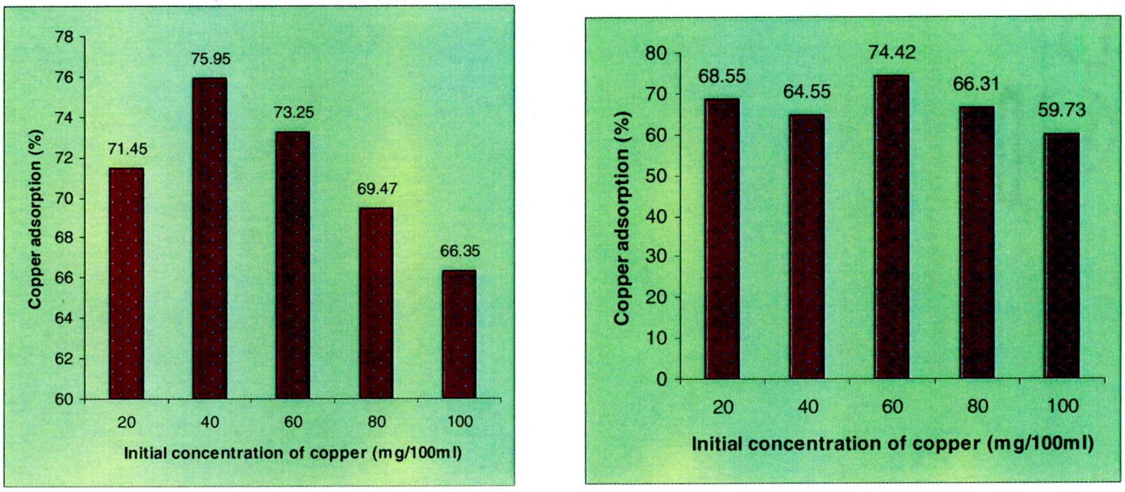
MEAN LEVELS OF COPPER IN THE SYNTHETIC SOLUTION AFTER ADSORPTION ON SELECTED AGROWASTES AT DIFFERENT INITIAL CONCENTRATIONS OF COPPER

Initial concentration (mg/100ml)	Copper levels (mg/100ml)		
	Orange peel	Rice husk	Sugarcane bagasse
20	5.71 (71.45)	06.29 (68.55)	7.10 (64.5)
40	9.62 (75.95)	14.18 (64.55)	17.22 (56.95)
60	16.05 (73.25)	15.35 (74.42)	22.33 (62.78)
80	24.42 (69.47)	33.69 (66.31)	30.32 (62.1)
100	33.65 (66.35)	43.27 (59.73)	40.38 (59.62)

The values in parentheses denote percentage adsorption of copper

Experimental condition
Dosage of adsorbent: 1g
pH: 5
Temperature: Room Temperature
Contact time: 4 hours

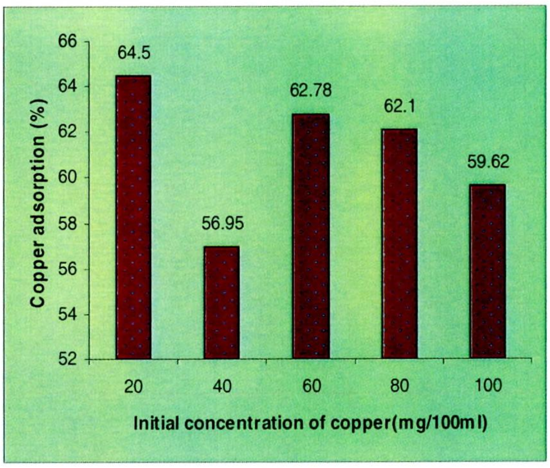
FIGURE 5
PERCENTAGE ADSORPTION OF COPPER FROM THE SYNTHETIC SOLUTIONS ON SELECTED AGROWASTES AT DIFFERENT INITIAL CONCENTRATIONS OF COPPER



Orange peel

Rice husk

Sugarcane bagasse



Oncel (2007) reported that the amount of copper adsorbed by Beidellite increased from 11.35-51.50 mg/g when the initial concentration was changed from 50-500 mg/l with an adsorbent dosage of 3g/l at pH 5.0

Gaballah *et al.* (1997) reported that the modified barks removed more than 90% of the copper cations from solutions having an initial concentration of 10ppm copper.

Ahamad *et al.* (2008) reported that more than 98% copper (II) was removed by saw dust in a concentration of 1x 10^{-3} M.

Goksungur *et al.* (2002) reported that with Baker's yeast, metal uptake values were 8.4, 21.1, 39.5, 72.4, 102.2, 120.7 and 109.3 mg / g with 10, 24.7, 48.3, 96.1, 145.7, 198.2 and 245.2 mg/l initial copper ion concentrations.

4.3 ADSORPTION ISOTHERM

The adsorption equilibrium data obtained for the removal of copper using the selected agrowastes were analyzed using Freundlich and Langmuir equations.

The Freundlich isotherm explains that the ratio of the amount of solute adsorbed on to a given mass of sorbent to the concentration of the solute in the solution is not a constant at different solution concentrations. The Langmuir isotherm is valid for monolayer sorption on a surface containing a finite number of binding sites. The treatment assumes uniform energies of sorbate in the plane of the surface (Brown *et al.,* 2000).

Tables 7, 8 and 9 show the different initial concentrations of copper with a constant adsorbent dose of 1g fitted to linearised Freundlich and Langmuir adsorption isotherm. The linearised form of equation is

$$\log x/m = \log k_f + 1/n \log Ce$$

where, x/m is the amount of the metal sorbed per unit weight of sorbent (mg/g), k_f is the measure of sorption capacity, 1/n is the measure of sorption intensity,

Ce is the equilibrium concentration of the residual metal ions in solution (Ramu *et al.,* 1992).

The linear plots of log 1/n versus Ce suggest the applicability of the Freundlich model for copper sorption. Figure 6 shows the plot of log x/m versus log Ce for copper. Figure 7 shows the plot of 1/(x/m) versus 1/Ce for copper removal using selected agrowastes.

The values of 1/n less than 1 are indicative of favourable adsorption (Anirudhan and Sreedhar, 1999). In the present investigation, the values of 1/n were found to be less than 1, which suggests the favourable adsorption behaviour of copper on selected agrowastes.

The linear plots of 1/(x/m) versus 1/Ce suggest the applicability of the Langmuir model, which is in the form

$$1/(x/m) = 1/q_o + 1/q_o(b) \text{ x } 1/Ce$$

where, x/m is the amount of copper adsorbed at equilibrium (mg/g), q_o and b are Langmuir constants related to the adsorption capacity and equilibrium constant respectively (Swamy *et al.,* 1998). The constants b and q_o can be evaluated from the intercept and slope of the linear plot of the experimental data of 1/(x/m) versus 1/Ce, respectively (Nagda *et al.,* 2007).

Based on the correlation coefficients (r), the equilibrium data was slightly better fitted in the Freundlich adsorption isotherm than the Langmuir equation. The higher value of n reflects the intensity of adsorption which signifies that the surface of biosorbents is heterogenous in nature and high enough for effective separation.

In the present study, the correlation coefficient (r) obtained by the regression analysis of Langmuir isotherm using orange peel, rice husk and sugarcane bagasse as adsorbents were found to be 0.9753, 0.9753 and 0.9661. The regression analysis of Freundlich isotherm using orange peel, rice husk and sugarcane bagasse were found to be 0.9753, 0.9167 and 0.9838.

TABLE 7

ADSORPTION OF COPPER ON ORANGE PEEL WITH VARYING INITIAL METAL CONCENTRATIONS

Initial concentration of copper (mg/100ml)	**Langmuir isotherm**		**Freundlich isotherm**			
	1/(x/m)	**1/Ce**	**Ce**	**x/m**	**Log Ce**	**Log x/m**
20	0.070	0.1751	5.71	14.29	0.7566	1.1550
40	O.0329	0.1040	9.62	30.38	0.9832	1.4826
60	0.0228	0.0623	16.05	43.95	1.2055	1.643
80	0.0180	0.0410	24.42	55.58	1.3877	1.7449
100	0.0150	0.0297	33.65	66.35	1.5270	1.8218
r	0.9753		0.9753			
1/n	0.83					

TABLE 8

ADSORPTION OF COPPER ON RICE HUSK WITH VARYING INITIAL METAL CONCENTRATIONS

Initial concentration of copper (mg/100ml)	**Langmuir isotherm**		**Freundlich isotherm**			
	1/(x/m)	**1/Ce**	**Ce**	**x/m**	**Log Ce**	**Log x/m**
20	0.0729	0.1590	6.29	13.71	0.7987	1.1370
40	0.0387	0.0705	14.18	25.82	1.1517	1.4120
60	0.0224	0.0651	15.35	44.65	1.1861	1.6498
80	0.0216	0.0297	33.69	46.31	1.5275	1.6657
100	0.0176	0.0231	43.27	56.73	1.6362	1.7538
r	0.9661		0.9167			
1/n	0.69					

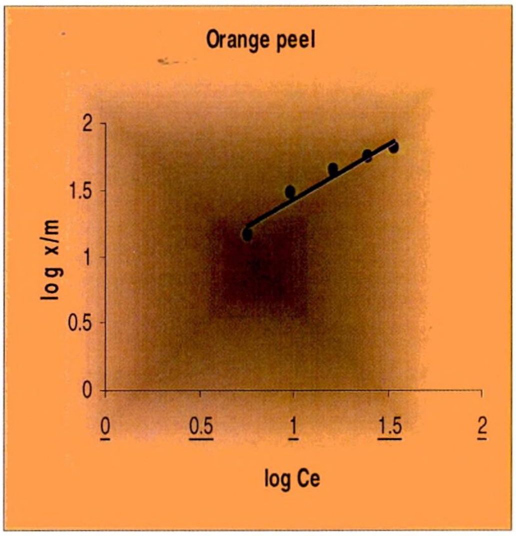
TABLE 9

ADSORPTION OF COPPER ON SUGARCANE BAGASSE WITH VARYING INITIAL METAL CONCENTRATIONS

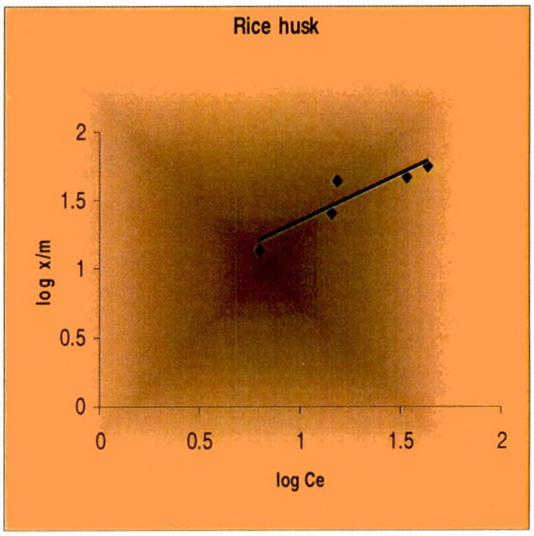
Initial concentration of copper (mg/100ml)	**Langmuir isotherm**		**Freundlich isotherm**			
	1/(x/m)	**1/Ce**	**Ce**	**x/m**	**Log Ce**	**Log x/m**
20	0.0775	0.1408	7.1	12.9	0.8513	1.1106
40	0.0439	0.0581	17.22	22.78	1.2360	1.3576
60	0.0265	0.0448	22.33	37.67	1.3489	1.5760
80	0.0201	0.0330	30.32	49.68	1.4817	1.6962
100	0.0168	0.0248	40.38	59.62	1.6062	1.7754
r	0.9833		0.9838			
1/n	0.92					

FIGURE 6
FREUNDLICH ADSORPTION PLOTS FOR THE SELECTED AGROWASTES AT DIFFERENT INITIAL COPPER CONCENTRATIONS

ORANGE PEEL



RICE HUSK



SUGARCANE BAGASSE

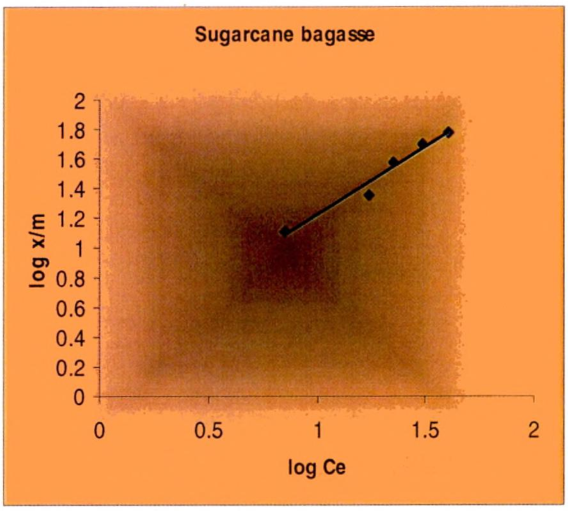
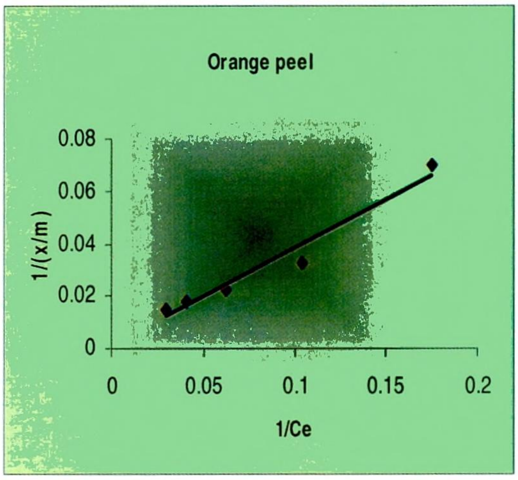
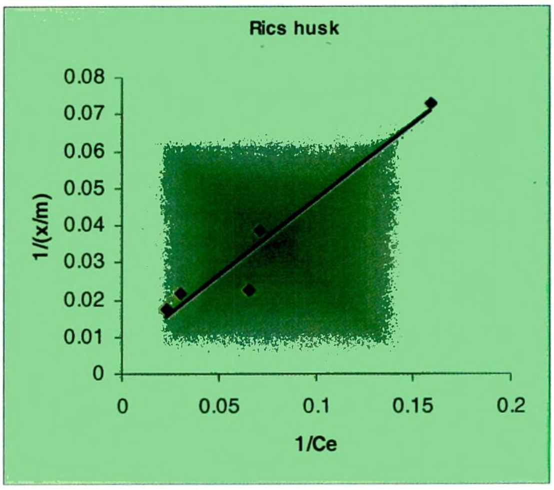


FIGURE 7
LANGMUIR ADSORPTION PLOTS FOR THE SELECTED AGROWASTES AT DIFFERENT INITIAL COPPER CONCENTRATIONS

ORANGE PEEL



RICE HUSK



SUGARCANE BAGASSE