DETOXIFICATION OF TOXIC METAL IONS BY SORPTION ONTO ACTIVATED CARBON FROM *HEVEA BRASILIENSIS* BARK – A COMPARATIVE STUDY

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ABSTRACT

Sorption of toxic metal ions (Ni^{2+}, Cu^{2+} and Cd^{2+}) from *Hevea brasiliensis* bark carbon (HBBC) was carried out at 30±1 °C under various experimental conditions. Effect of various process parameters has been investigated by following the batch adsorption technique at 30 ± 1°C. The percentage removal increased with decrease in initial concentration and particle size and increase in contact time and dose of adsorbent. As initial pH of the slurry increased, the percentage removal increased, reached a maximum. The adsorption is highly pH sensitive. Adsorption data were modelled with various isotherms and first order kinetic equations proposed by Natarajan-Khalaf, Lagergren and Bhattacharya-Venkobachar and intraparticle diffusion models found to be applicable. Kinetics of adsorption is observed to be first order with Intra- particle diffusion as one of the rate determining steps. The monolayer adsorption capacities of HBBC also studied by Langmuir isotherms. HBBC could be used as low-cost adsorbents in effluent treatment, especially for the removal of metal ions, particular in Ni^{2+}, Cu^{2+} and Cd^{2+} ions. It is confirmed by FT-IR studies before and after adsorption.

KEYWORDS: Toxic metal ions, *Hevea brasiliensis* bark carbon, adsorption, kinetic equations, intra-particle diffusion.

INTRODUCTION

As a modern world, the increase of industrial activities has intensified environmental pollution problems and the deterioration of several ecosystems with the accumulation of pollutants, especially heavy metals. Effluents containing heavy metals are discharged from various industrial processes. According to World Health Organization (WHO) the metals of the most immediate concern are copper, cadmium, nickel, mercury, lead, chromium, manganese, zinc and aluminium. All toxic metal ions (Nickel, copper and cadmium) have received a great deal of attention. These metals may be found in wastewater discharges from the plating industry, the manufacture of cadmium-nickel batteries, fertilizers, pesticides, lead mining, pigments dyes and textile operations (Salim *et al.,* 1992; Grayson and Othumer, 1978). The major ill-effects caused by metal ions are erythrocyte destruction, dermatitis, inhibition of enzyme activity, head ache, Wilkinson disease, dizziness, nausea and vomiting, chest pain, tightness of chest, dry cough, shortness of breath, rapid respiration, nephritis, cyanosis and extreme weakness. The use of activated carbon for the removal of the toxic metal ionic pollutants present in low concentration in aqueous solution is of considerable importance. Activated Carbon (AC) adsorption is being widely used in effluent treatment. Because of high cost of commercial AC (CAC) and difficulty in its procurement low-cost adsorbents alternative to CAC are to be developed from abundant agricultural wastes (Annadurai and Krishnan, 1996). This has necessitated the titled investigation to find out the suitability of *Hevea brasiliensis* bark carbon for the removal of toxic metal ions (Ni^{2+}, Cu^{2+} and Cd^{2+}). The objectives of this study is to indigenously prepare AC (IPAC) from *Hevea brasiliensis* bark to study the effect of various process parameters

on the extent of removal of these toxic metal ions and to model the adsorption data with various isotherms, first order kinetic equations and intra-particle diffusion model.

MATERIAL AND METHOD
Materials
Hevea brasiliensis bark was carbonized with sodium bicarbonate at 300-400°C and kept at 600°C in a muffle furnace (Neolab, India) to get carbon. The carbon was sieved (90, 125, 150, 180, 210, 250 micron), activated by acid digestion (4 N HNO_3; 2hr at 80°C) and dried in an air – oven (at 120°C for 2hr). Batch type adsorption studies were carried out (Kadirvelu and Namasivayam, 2003) under various experimental conditions. Nickel ammonium sulphate (AR), Cupric sulphate (AR) and Cadmium nitrate (AR) were suitably diluted individually with deionised water and estimated by sodium salt of ethylenediaminetetraacetic acid (EDTA) using murexide, Fast Sulphon Black-F and xylenol orange. Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode (Kannan, 1991). Toxic metal (Ni^{2+}, Cu^{2+} and Cd^{2+}) ions concentration were estimated complexometric titration as per the literature methods (Jeffery *et al.*, 1991). Effect of various process parameters on the extent of removal of toxic metal ions was studied. The data were analysed statistically and interpreted.

Adsorption experiments
Adsorption experiments were carried out at room temperature (30±1 °C) under batch mode. Stock solution of metal salts (AR) were prepared suitably diluted with DD water and estimated by EDTA method using (Jeffery *et al.*, 1991) indicators. Exactly 50mL of metal ion solution of known initial concentration was shaken with a required dose of adsorbent (HBBC =2-20 g L^{-1}) of a fixed particle size (HBBC=90-250 micron) in a thermostatic orbit incubator shaker (Neolab, India) at 200 rpm after noting down the initial pH of the solution (pH = 6.1 for Ni^{2+}; 7 for Cu^{2+} and Cd^{2+}). The initial pH was adjusted to the required pH value (range: 2-10) by adding either 1 M HCl or 1 M NaOH solution. After equilibration, the final concentrations (C_e) were also estimated complexometrically (Jeffery *et al.*, 1991). The value of percentage removal and amount adsorbed (Kannan and Rajakumar, 2003) were calculated using the following relationships:

Percentage removal = 100 ($C_i – C_e$) / C_i (Eq. 1)

Amount adsorbed (q) = ($C_i – C_e$) / m   (Eq. 2)

where, C_i and C_e are initial and equilibrium (final) concentration of toxic metal ions (ppm), respectively and m is the mass of adsorbent, in g L^{-1}.

FT-IR spectra were recorded as KBr pellets utilizing a SHIMADZU FT-IR 410 spectrometer.

RESULTS AND DISCUSSION
Instrumentation techniques
FT-IR spectra were recorded for the AC samples with and without Ni^{2+}, Cu^{2+} and Cd^{2+} loading. The characteristic group frequencies ($\bar{v}$, in cm^{-1}) observed for various surface functional groups are shown in Table 1. The FT-IR spectra of various carbons and metal ion-loaded HBBC are almost similar with slight shift in frequencies (Sharma, 1980).

The surface functional groups are almost common as revealed by some common peaks, which appeared at 3412-3461, 2829-2945, 1612-1821, 1430-1576, 615-687 and 1240-1504 cm^{-1}; depending upon the nature and type of raw materials. The characteristic peaks are slightly varying in their position for different IPAC. A peak around 1800-1600 cm^{-1} in HBBC confirms the presence of carbonyl group. This was further evidenced by another peak around 1650-1675 cm^{-1}, which reveals the keto nature. The peak around 3400-3550 cm^{-1} confirms the presence of -OH group. The functional groups may be –COOH and/or –OH. The IR peaks around 1200-1500 cm^{-1} may be due to the stretching vibrations of lactone (γ and / or δ), =C-O, -CH= and -CH_2- functional groups. The IR spectra indicate the presence of surface functional groups like C=O, -COOH, -OH, -CO-O-CO-, -C-O-C-, *etc.,* and their involvement in the adsorption process.

Table 1. FT-IR Spectroscopic characteristic frequencies ($\bar{\nu}$ in cm^{-1}) of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC - before and after adsorption of Toxic metal ions*

Assignment	Ni^{2+}	Cu^{2+}	Cd^{2+}
O-H stretching	3402 *(3350)	3411 (3351)	3410 (3448)
C-H stretching	2922 (2818)	2934 (2915)	2941 (2833)
C=O stretching	1715 (1712)	1611 (1609)	1655 (1623)
CH$_2$ bending	1461 (1412)	1535 (1498)	1422 (1418)
C-S stretching	605 (679)	636 (656)	610 (626)
C-O-C stretching	1033 (1052)	1004 (1041)	1021 (1031)

* Values in parentheses are for Ni^{2+}, Cu^{2+} and Cd^{2+} ions-loaded carbon.

Effect of Process parameters

The adsorption experiments were carried out at different experimental conditions (Table 2) and the results obtained are discussed below:

Effect of initial concentration

The results on the extent of removal of toxic metal ions under various experimental conditions are given in Table 2. The percentage removal (% R) decreased with increase in initial concentration, due to the limited number of available active sites on the surface of HBBC to accommodate higher concentration of toxic metal ions (Ni^{2+}, Cu^{2+} and Cd^{2+}) (Kannan and Rajakumar, 2003). The effect of initial concentration is shown in Figure 1.
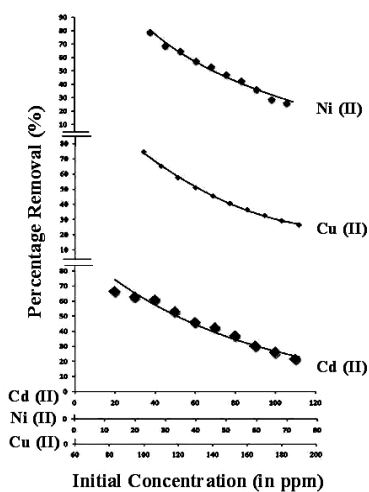

Figure 1. Effect of initial concentration for the removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC

Adsorption isotherms

Adsorption data were fitted with Freundlich and Langmuir isotherms (Kannan and Rajakumar, 2003) by carrying out the correlation analysis. The results are given in Table 3. The observed r-values close to unity indicate the applicability of these two isotherms. HBBC, as evidenced from Q$_o$ (monolayer adsorption capacity, in mg g^{-1}) values.

Freundlich isotherm: log q = log K + (1/n) log C$_e$ (Eq. 3)

Langmuir isotherm : (C$_e$/q) = (1/Q$_o$b) + (C$_e$/Q$_o$)   (Eq. 4)

where, K and 1/n are the measures of adsorption capacity and intensity of adsorption, respectively; q is the amount adsorbed per unit mass of adsorbent (in mg g^{-1}); Q$_o$ and b are Langmuir constants,

which are the measures of monolayer adsorption capacity (in mg g^{-1}) and surface energy (mg L^{-1}), respectively.

Table 2. Effect of initial concentration for the extent of removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto   HBBC at 30±1 °C

Process Parameter	Range	Percentage Removal		
		Ni^{2+}	Cu^{2+}	Cd^{2+}
Initial conc. (ppm)	25-70 (Ni^{2+}) 100-190 (Cu^{2+}) 20-110 (Cd^{2+})	79-26 *(1.6-1.5)	75-26 (6.2-4.2)	66-21 (1.1-2.0)
Contact time (min)	5-55	19-58 (0.8-2.4)	13-40 (1.7-5.4)	12-60 (0.7-3.5)
Dose (g L^{-1})	2-20	30-74 (1.2-3.1)	17-56 (2.2-7.5)	28-60 (1.6-3.5)
Initial pH	2-10	26-72 (1.1-3.0)	25-60 (3.3-8.0)	20-82 (1.2-4.8)
Particle size (μm)	90-250	58-11 (2.4-0.5)	40-9 (5.4-1.2)	60-23 (3.5-1.3)

* Values in parentheses are amount adsorbed for Ni^{2+}, Cu^{2+} and Cd^{2+} ions.

Table 3. Adsorption isotherm data for removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC at 30±1 °C

Model Parameter	Toxic metal ions		
	Ni^{2+}	Cu^{2+}	Cd^{2+}
Freundlich isotherm			
slope (1/n)	0.108	1.050	0.381
Intercept (log K)	0.143	0.175	0.216
r – value	0.920	0.973	0.943
Δq (%)	0.031	0.016	0.358
Langmuir isotherm			
Slope (1/Q$_o$)	0.488	0.220	0.335
Intercept (1/Q$_o$b)	0.625	2.047	3.207
r – value	0.999	0.997	0.996
Q$_o$ (mg g^{-1})	2.051	4.546	2.981
b (g L^{-1})	0.780	0.107	0.105
R$_L$ value	0.033	0.079	0.183
Δq (%)	0.025	0.174	0.147

In order to compare the validity of each model (isotherm) more efficiently a normalised standard deviation, Δq(%) is calculated using the following equation:

$$\Delta q\ (\%) = 100 \times \{\ (\ \textstyle\sum [\ (\ q_t^{exp.} - q_t^{cal.}\ ) / q_t^{exp.}\ ]^2)\ /\ (n - 1)\ \}^{1/2} \qquad \text{(Eq. 5)}$$

where, the superscripts, exp. and cal. are the experimental and calculated values of q$_t$ *viz.*, the amount adsorbed at different time t and n is the number of observations. The Δq(%) values are also given in Table 3. Based on the low values of Δq(%), it is concluded that the adsorption of toxic metal ions can be best described by the Langmuir adsorption isotherm. The monolayer adsorption capacities (Q$_o$) of the adsorbents are found to be of the order given below:

$$Cu^{2+} >> Cd^{2+} > Ni^{2+}$$

Further, the essential characteristics of the Langmuir isotherm can be described by a **Separation factor, R$_L$**, which is defined by the following equation:

$$R_L = [\ 1\ /\ (\ 1 + bC_i\ )\ ] \qquad \text{(Eq. 6)}$$

where, C$_i$ = optimum initial concentration of Ni^{2+}, Cu^{2+} and Cd^{2+} ions (in mg L^{-1})
       b = Langmuir constant (in L mg^{-1})

The values of **separation factor**, R_L indicate the nature of the adsorption process as given below:

R_L values	Nature of adsorption process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the present study, the computed values of R_L (Table 2) are found to be fraction in the range of 0-1 (0.033 for Ni^{2+}, 0.079 for Cu^{2+} and 0.183 for Cd^{2+} ions), indicating that the adsorption process is favorable for this adsorbent (HBBC) for the removal of toxic metal ions.

Effect of contact time
The % R increases with increase in contact time (40 min., for Ni^{2+}; 35 min., for Cu^{2+} and Cd^{2+}) due to more amounts of Ni^{2+}, Cu^{2+} and Cd^{2+} ions removed due to effective contact and due to the availability of active sites. The effect of contact time is shown in Figure 2. At the initial stage, the rate of removal of toxic metal ions was higher, due to the availability of more than the required number of active sites on the surface of carbons and became slower at the later stages of contact time, due to the decreased or lesser number of active sites. Similar results have been reported in literature for the removal of dyes (Kannan and Meenakshi Sundaram, 2002), organic acids and metal ions (Kannan and Veemaraj, 2009) by various adsorbents.
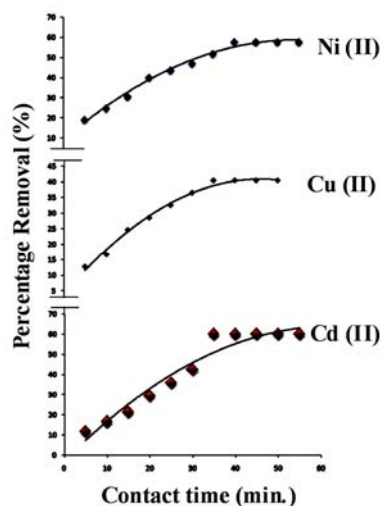

Figure 2. Effect of contact time for the removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC

Kinetics of adsorption
The first order kinetic equations like Natarajan-Khalaf (Raji *et al.,* 1986), Lagergren (Lagergren, 1898) and Bhattacharya-Venkobachar (Bhattacharya and Venkobachar, 1984) equations were applied to the adsorption data (Table 4).

Natarajan and Khalaf equation:	$Log (C_i / C_t) = (k / 2.303) t$	(Eq. 7)
Lagergren equation:	$Log (q_e - q_t) = log\ q_e - (k / 2.303) t$	(Eq. 8)
Bhattacharya and Venkobachar equation:	$Log [1 - U (T)] = - (k / 2.303) t$	(Eq. 9)

where,
C_i and C_t = concentration of Ni^{2+}, Cu^{2+} and Cd^{2+} ions at time zero and time t, respectively (in mg L^{-1})
q_e and q_t = amount of Ni^{2+}, Cu^{2+} and Cd^{2+} ions adsorbed at equilibrium time and time t, respectively (in mg g^{-1})
$U (T)$ = $[(C_i - C_t) / (C_i - C_e)]$
C_e = equilibrium Ni^{2+}, Cu^{2+} and Cd^{2+} ions concentration (in mg L^{-1})
k = first order adsorption rate constant (in $min.^{-1}$)

The r-values (correlation coefficient close to unity) indicate the applicability of these kinetic equations and the first order nature of adsorption of Ni^{2+}, Cu^{2+} and Cd^{2+} ions on HBBC. The rate of adsorption of Ni^{2+}, Cu^{2+} and Cd^{2+} ions is calculated. The presence of intra- particle diffusion as the rate limiting step was tested by applying the intra- particle diffusion model.

$$q_t = k_p \, t^{1/2} + c \tag{Eq. 10}$$

The higher value of k_p (k_p values = Ni^{2+}=0.385; Cu^{2+}=1.033; Cd^{2+}=0.702) indicate that HBBC are highly porous in nature. The value of intercept (c) give an idea about the boundary layer thickness, *i.e.,* larger the intercept (Ni^{2+}>Cu^{2+}>Cd^{2+}), greater is the boundary layer effect (Rajakumar, 2002).

Table 4. Kinetics of adsorption for removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC at 30±1 °C

Model Parameter	Ni^{2+}	Cu^{2+}	Cd^{2+}
Natarajan-Khalaf eqn.			
$10^2 \, k$ (min.$^{-1}$)	0.018	0.013	0.024
r - value	0.995	0.997	0.942
Δq (%)	9.270	7.517	5.268
Lagergren eqn.			
$10^2 \, k$ (min.$^{-1}$)	0.051	0.059	0.030
r – value	0.972	0.987	0.980
Δq (%)	1.817	0.699	1.610
Bhattacharya-Venkobachar eqn.			
$10^2 \, k$ (min.$^{-1}$)	0.051	0.059	0.030
r – value	0.972	0.987	0.980
Δq (%)	21.694	18.791	33.460
Intra-particle diffusion model			
k_p (mg g^{-1} min.$^{-1/2}$.)	0.385	1.033	0.702
Intercept (*c*)	0.127	0.799	1.216
r – value	0.994	0.995	0.945
Δq (%)	0.241	0.404	4.873
Log (*%R*) *vs* Log(*time*)			
slope	0.535	0.619	0.806
r – value	0.993	0.993	0.975
Δq (%)	38.358	56.997	45.003

The values of log (% R) are found to be linearly correlated (r values Ni^{2+}=0.993; Cu^{2+}=0.993 and Cd^{2+}=0.975) with log (time), with slope values are greater than 0.5 (slope: Ni^{2+}=0.535; Cu^{2+}=0.619 and Cd^{2+}=0.806). This indicates that besides the intra- particle diffusion, there may be other processes controlling the rate of adsorption, all of which may be operating simultaneously. The results of the present study conclude that HBBC could be used as low-cost adsorbent in effluent treatment, especially for the removal of toxic metal ions.

Effect of dose of adsorbent
The % R increased with increase in dose of adsorbent owing to the increase in surface area and number of active sites for the adsorption of Ni^{2+}, Cu^{2+} and Cd^{2+} ions or due to the conglomeration of carbons at higher doses (Periasamy and Namasivayam, 1996; Kannan and Meenakshisundaram, 2002). The effect of dose is shown in Figure 3.

The relative increase in the percentage removal of toxic metal ions is found to be insignificant after a dose of 20 g L^{-1} of HBBC, which is fixed as the optimum dose. The values of log (% R) are also found to be linearly correlated with log (dose) values. The values of log (% R) are found to be linearly correlated to log (dose) with correlation coefficients, which are almost unity (r values Ni^{2+}=0.999; Cu^{2+}=0.985 and Cd^{2+}=0.935).

This suggests that the adsorbed toxic metal ions (Ni^{2+}, Cu^{2+} and Cd^{2+} ions) may either block the access to the internal pores of carbons or may cause particles to aggregate and thereby minimizing

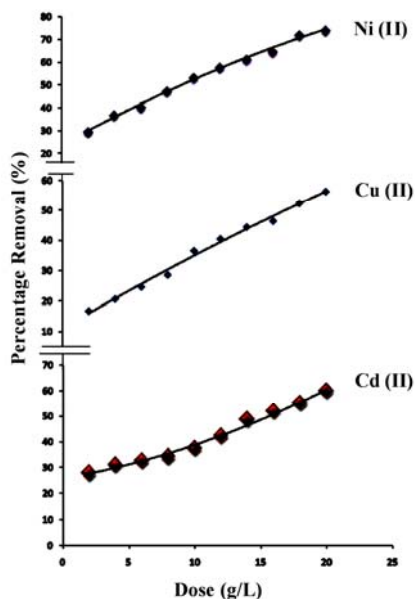the availability of active sites for adsorption (Periasamy and Namasivayam, 1996; Kannan and Veemaraj, 2009).

Figure 3. Effect of dose for the removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC

Effect of initial pH
As initial pH increases, the extent of removal (% R), increases reaches a maximum value (Kannan and Veemaraj, 2009). The effect of initial pH is shown in Figure 4. The optimum pH for removal of Ni^{2+} ions is fixed as 6.1 and Cu^{2+} and Cd^{2+} ions are fixed as 7.0. The near neutral pH is found to be favourable. The pH value slightly decreases and change in pH (ΔpH = initial pH - final pH) values after adsorption are found to decrease in the order of 0.3-0.5 units (Kannan and Raja Kumar, 2003). This suggests that during the adsorption of nickel species, protons are released from the surface functional groups like phenolic, carboxylic and enolic groups present on the carbons.
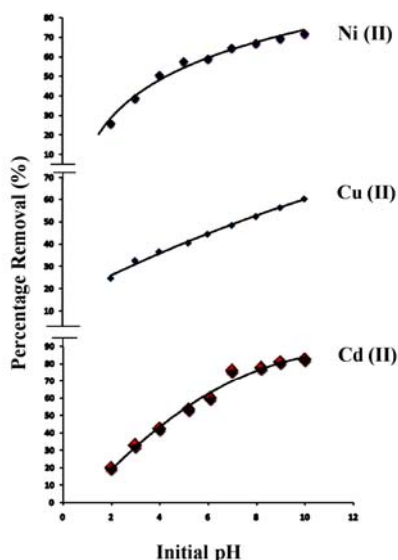

Figure 4. Effect of pH for the removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC

Effect of particle size
The amount of toxic metal ions adsorbed increases with decrease in particle size of the adsorbent (Kannan and Rajakumar, 2003). The effect of particle size is shown in Figure 5. This is due to the availability of surface area with the decrease in particle size.
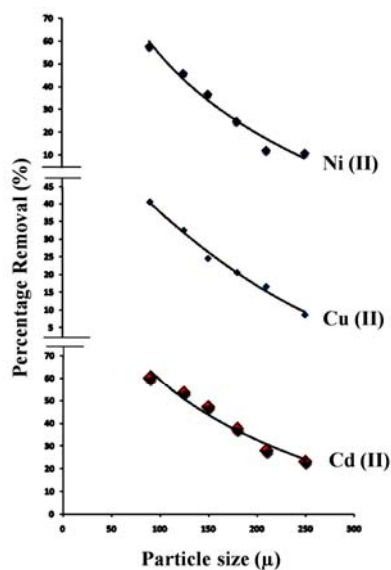
Figure 5. Effect of particle size for the removal of Ni^{2+}, Cu^{2+} and Cd^{2+} onto HBBC

The optimum conditions fixed for the effective removal of nickel (II) ions are: C_i = 25 ppm for Ni^{2+}; 100 ppm for Cu^{2+} and 20 ppm for Cd^{2+}; contact time = 40 min., for Ni^{2+}; 35 min., for Cu^{2+} and Cd^{2+}; dose = 20 g L^{-1} for Cd^{2+} and 12 g L^{-1} for Ni^{2+} and Cu^{2+}; particle size = 90 micron and pH = 6.1 for Ni^{2+} and 7.0 for Cu^{2+} and Cd^{2+} at 200 rpm speed and 30±1 °C.

CONCLUSION

Adsorbate species are found to adsorb strongly on the surface of HBBC. The faster adsorption kinetic data may be useful for environmental technologists in designing Ni^{2+}, Cu^{2+} and Cd^{2+} containing waste water. The adsorption process is found to be first order with intra-particle diffusion as one of the rate determining steps. HBBC possess the maximum adsorption capacity and hence, it is an effective adsorbent for the removal of toxic metal ions like Ni^{2+}, Cu^{2+} and Cd^{2+}, HBBC could be considered as cost-effective adsorbent and useful for the economic treatment of waste water containing Ni^{2+}, Cu^{2+} and Cd^{2+} to use an agricultural material *Hevea brasiliensis* bark as an adsorbents

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