Removal of Ni²⁺, Cu²⁺ and Zn²⁺ Using Different Agricultural Residues: Kinetics, Isotherm Modeling and Mechanism *via* Chemical Blocking

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Four different combinations, prepared by mixing various amounts of *Trifolium alexandrinum* biomass powder (TABP), *Arachis hypogea* shell powder (AHSP) and *Eucalyptus cameldulensis* saw dust (ESCD) were studied for the removal of Ni²⁺, Cu²⁺ and Zn²⁺ from aqueous solutions. The highest adsorption capacity of Ni²⁺, Cu²⁺ and Zn²⁺ was found to be 92.52, 94.12 and 96.75 mg g⁻¹, respectively. The adsorption kinetics of all the three metals were relatively fast attaining the equilibrium within 300 min and were best described by pseudo-second order kinetics. The adsorption equilibrium followed Freundlich and Langmuir adsorption isotherm models. The FTIR study revealed that carboxyl and hydroxyl functional groups were mostly accountable for the removal of Ni²⁺, Cu²⁺ and Zn²⁺. The blocking of carboxyl and hydroxyl groups of the combination A [TABP (30%) + ESCD (35 %) + AHSP (35 %)] was done and it was found that more than 70 % removal of Ni²⁺, Cu²⁺ and Zn²⁺ were due to the contribution of carboxylic group, whereas less than 30 % removal of the same metal ions were due to the hydroxyl group. The release of Na⁺, K⁺, Mg²⁺, Ca²⁺ and H⁺ from the combination A with the equivalent uptake of Ni²⁺, Cu²⁺ and Zn²⁺ supported ion exchange as the foremost mechanism of adsorption. The column studies were carried out with electroplating wastewater containing Ni²⁺, Cu²⁺ and Zn²⁺ metal ions. Thomas model was applied to evaluate the metal uptake capacity for Ni²⁺, Cu²⁺ and Zn²⁺ and at the breakthrough points, the columns were recharged using 0.1 M HCl for three successive sorption-desorption cycles without much loss in the initial sorption capacity of the combination used. In brief, it can be concluded that the adsorbents used in different combinations are attractive and are alternative options for desalinating the heavy metal from industrial effluents.

Key Words: *Trifolium alexandrinum*, *Arachis hypogea*, *Eucalyptus cameldulensis*, Chemical blocking, Ion exchange mechanism.

INTRODUCTION

Heavy metals discharged from various industries such as metal plating, mining, tanneries, painting and car radiator manufacturing are the major cause of water contamination. Utmost attention is being paid to the health hazards presented by the existence of heavy metal ions, *viz*., Ni, Cu, Zn, Pb, Cd and Hg. The high concentration of these metal ions could be extremely harmful to humans, animals and plants mainly due to their accumulation in biological system[1]. Moreover unlike organic pollutants, the majority of which are liable to biological degradation, metal ions do not degrade into harmless end products making them more dangerous[2]. The removal of heavy metal in an effective manner from water and wastewater is, thus, ecologically very important. There are many reported and conventional technologies for the removal and recovery of metals from wastewater, which include chemical precipitation[3], flotation[4], biosorption[5-7], electrolytic recovery, membrane

separation[8], removal by adsorption on minerals[9,10] and activated carbon adsorption[11,12]. In spite of the fertile use of activated carbon, it remains an expensive material to be used for adsorption. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters[13]. Therefore this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency. In recent years, the search for low-cost adsorbents that have metal binding capacities has intensified. Agricultural by-products have been extensively studied for metal removal and recovery from wastewater[14-16].

In present work, the adsorption of Ni²⁺, Cu²⁺ and Zn²⁺ from synthetic solution was done in batch mode using four different combinations, obtained by mixing *Trifolium alexandrinum* biomass powder, *Eucalyptus cameldulensis* saw dust and *Arachis hypogea* shell powder. The influence of pH, initial metal ion concentration and contact time were studied and the experimental data obtained were evaluated and fitted

using equilibrium isotherms and kinetic models. Mechanistic aspect of metal adsorption were investigated using different experimental approaches such as FTIR studies, chemical blocking of the functional groups and the release of alkali and alkaline earth metals during adsorption of the metal ions in an ion exchange process. Under optimized conditions, column studies were conducted using the electroplating industrial wastewater containing Ni^{2+}, Cu^{2+} and Zn^{2+} and metal uptake capacity was evaluated using Thomas model.

EXPERIMENTAL

The quantification of the metal ions (Ni^{2+}, Cu^{2+} and Zn^{2+}) in the solutions has been performed on atomic absorption spectrophotometer (AAS) AA630, Shimadzu. Fourier Transform-Infra Red (FT-IR) spectra of the adsorbents have been recorded on Thermo, Nicolet is 10 FT-IR spectrophotometer. The pH of the solution has been measured by Cyber scan, Eutch pH meter and the orbital shaker incubator by Metrex scientific instruments has been used for shaking the samples during batch operations at desired temperature and agitation speed. Software Sigma plot 11 has been used for the data analysis and fitting the experimental data in Thomas model.

Adsorbents collection and preparation: *Trifolium alexandrinum* biomass, *Eucalyptus cameldulensis* saw dust and *Arachis hypogea* shells were collected form Jagadhri, Haryana, India. All three agricultural residues were washed extensively with deionized water to remove dirt and other particulate matter and then dried in the sun light for 7 days. *Trifolium alexandrinum* biomass and *Arachis hypogea* shells were finally grinded separately, in a vegetable grinder to obtain the biomass powder. Resulting powders were sieved through a 600 µm mesh sized sieve and powder (500 g each) thus obtained was heated in an electric hot air oven at 105 ºC for 12 h. The dried *Trifolium alexandrinum* biomass powder (TABP), *Eucalyptus cameldulensis* saw dust (ECSD) and *Arachis hypogea* shell powder (AHSP) were mixed in different wt % as mentioned in Table-1 to prepare the various combinations (A to D). The various combinations were prepared in order to enhance the adsorption capacity of the adsorbents for multi metal ion solutions, where single adsorbent fails to adsorb all the metal ions up to good extend.

| TABLE-1 |
| DIFFERENT COMBINATIONS OF TABP, ECSD AND AHSP |

Combinations	Agricultural residues (wt %)
A	TABP (30) + ECSD (35) + AHSP (35)
B	AHSP (50) + ECSD (50)
C	TABP (50) + AHSP (50)
D	ECSD (50) + TABP (50)

Preparation of stock solutions: An aqueous stock solutions (1000 mg L^{-1}) of Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions were prepared by dissolving requisite amount of nickel nitrate, copper chloride and zinc sulphate (AR, Loba Chemie, India) in 1 L deionized water, respectively. The stock solutions were further diluted with deionized water to prepare the solutions of the desired concentrations. The pH of the solutions was adjusted by adding the appropriate amounts of 0.1 M HCl or 0.1 M NaOH solutions.

Batch studies: Batch experiments for Ni^{2+}, Cu^{2+} and Zn^{2+} biosorption from synthetic solutions were carried out at different pH values *viz.*, 2.0-7.0 for all the metal ions by agitating 1.0 g each of the four different combinations (A to D) in 250 mL screw-cap conical flasks with 100 mL of metal ion solutions, respectively. The mixture so obtained was agitated in orbital shaker at 225 agitation speed for 300 min at 30 ºC. After every 20 min of agitation, 2 mL of the suspensions were centrifuged at 5000 rpm for 10 min and analyzed using AAS. Under optimized conditions, the effect of initial metal ion concentration from 25 to 200 mg L^{-1} and contact time from 1 to 300 min has been studied.

The per cent of the metal removal (R %) was calculated for each experiment using eqn. 1

$$R\,(\%) = \left[\frac{(C_i - C_e)}{C_i} \right] \times 100 \qquad (1)$$

where C_i and C_e were the initial and equilibrium concentrations of Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions in the solution, respectively. The metal biosorption capacity (q_e = mg g^{-1}) of each combination for biosorption of Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions at equilibrium was determined using eqn. 2.

$$q_e = \frac{(C_i - C_e)}{M_a} \times V \qquad (2)$$

where V is the volume of the solution (L) and M_a is the mass of the biosorbent (g) used.

Ion exchange capacity of the combination A: Among all the four combinations studied, combination A showed maximum removal for all the three metal ions in the batch studies and the ion exchange capacity of the same was evaluated. The release of Na^+, K^+, Mg^{2+}, Ca^{2+} and H^+ ions from 0.1 M HCl washed combination A was used to verify its estimated ion exchange capacity. 1 g of combination A was contacted with 100 mL (0.1 M HCl) and the mixture was stirred on the magnetic stirrer for 1 h at 30 ºC. Then it was centrifuged at 5000 rpm for 10 min. The residue obtained was recontacted in fresh 100 mL (0.1 M HCl) and the process was repeated twice. The filtrates so obtained were analyzed for the release of Na^+, K^+, Mg^{2+}, Ca^{2+} and H^+ using atomic absorption spectrophotometer. The deionized water replaced HCl in the similar procedure and was used as the control.

Blocking of carboxyl and hydroxyl functional groups: In order to quantify the role of carboxyl (-COOH) and hydroxyl (-OH) in metal sorption, they were blocked in combination A. Carboxyl group was protected by treating combination A with methanol[17] as given in eqn. 3.

$$RCOOH + CH_3OH \rightarrow RCOOCH_3 + H_2O \qquad (3)$$

To block the carboxylic group, 9 g of the combination A was treated with anhydrous CH_3OH (633 mL) in presence of 5.4 mL HCl (5.0 M), with continuous stirring on magnetic stirrer at 225 rpm for 6 h. The combination A residue was then separated by centrifugation and washed thrice with deionised water to remove excess CH_3OH and HCl. The final biomass obtained was dried in hot air oven at 105 ºC for 12 h and stored for further use.

Hydroxyl group of sorbent was protected by treating combination A with formaldehyde[18] as given in eqn. 4.

$$2R-OH + HCHO \rightarrow (R-O)_2CH_2 + H_2O \qquad (4)$$
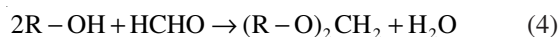
In a typical experiment, 5 g of the combination A was treated with HCHO (100 mL) under agitation on magnetic stirrer at 225 rpm for 6 h. The residual biomass was then separated and further processed and stored following the same method as mentioned for the carboxylic group protection.

Characterization of electroplating industrial wastewater: Electroplating industrial wastewater was collected from the electroplating unit situated in Karnal, Haryana (India) and analyzed for Ni²⁺, Cu²⁺ and Zn²⁺ metal ions as given in Table-2. The collected wastewater was desalinated using combination A in column studies in a pilot experiment and same could be enlarged even at industrial level.

TABLE-2
CHARACTERISTICS OF THE ELECTROPLATING
INDUSTRIAL WASTEWATER

Concentration of heavy metal and anions (mg L⁻¹)					
Ni²⁺	Cu²⁺	Zn²⁺	Cl⁻	SO₄²⁻	NO₃⁻
119.15	137.35	105.23	166.78	208.22	98.78
pH = 6.0, turbidity (NTU) = 36.32.					

Column studies using electroplating industrial wastewater: Three glass columns (1, 2 and 3) having 50 cm length and 2.5 cm internal diameter were packed with bed depth of 12 cm by taking 10 g of the combination A. The schematic diagram of the experimental set-up is shown in Fig. 1. The process was operated in down-flow mode at room temperature (30 °C). To stabilize the process, before each run, 1 L deionized water adjusted to pH 6, 5 and 4 was passed through the columns 1, 2 and 3, respectively for 12 h at a flow rate of 2.5 mL min⁻¹ using peristaltic pump. Then the electroplating wastewater containing Ni²⁺, Cu²⁺ and Zn²⁺ metal ions with pH 6 was passed through the column 1 at the same flow rate. To measure the concentrations of the metal ions in the effluents of each column, 5 mL samples of the effluents were intermittently collected after 20 min and analyzed using atomic absorption spectrophotometer. The percolation of the wastewater into each column was stopped as soon as the breakthrough point (BTP) in that particular column was achieved. Breakthrough occurs when the effluent concentration from the column is *ca.* 3-5 % of the influent concentration[19]. Effluent of the column 1 was readjusted to pH 5 using a 0.1 M HCl solution and then passed through the column 2. On achieving the breakthrough point in column 2, finally the effluent pH was changed to 4 and was passed through the column 3. The columns were regenerated using 0.1 M HCl. The wastewater was treated till the concentration of all the metal ions reached to satisfy the Central Pollution Control Board standards[20].

Column regeneration studies: The removal of the adsorbed metals from the biomass is required for safer biomass disposal, unless the metal-laden biomass is to be utilized as an alternative product. For desorption of Ni²⁺, Cu²⁺ and Zn²⁺ metal ions bound on the biomass, 1 L of 0.1 M HCl solution was circulated through each column at flow rate of 2.5 mL min⁻¹ for 12 h at the breakthrough point (BTP). Three cycles of sorption followed by desorption were carried out to assess the reusability potential of the adsorbent.
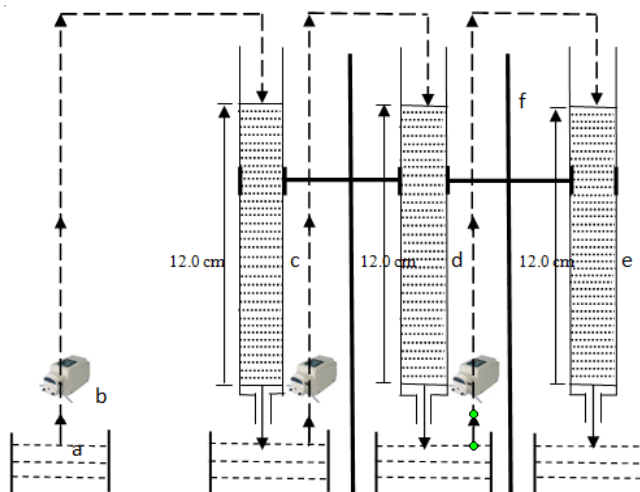

Fig. 1. Schematic diagram of column experimental set-up for the removal of Ni²⁺, Cu²⁺ and Zn²⁺ from electroplating waste water (a = electroplating wastewater containing Ni²⁺, Cu²⁺ and Zn²⁺, b = peristaltic pump, c, d, e = column 1, 2 and 3, respectively, f = column holding stand)

RESULTS AND DISCUSSION

FTIR studies: In order to determine the main functional groups responsible for the biosorption of Ni²⁺, Cu²⁺ and Zn²⁺ from the industrial wastewater in column studies, the combination A was recovered separately from the all three columns, dried and subjected to the FTIR studies. The recorder spectra have been compared as shown in Fig. 2.
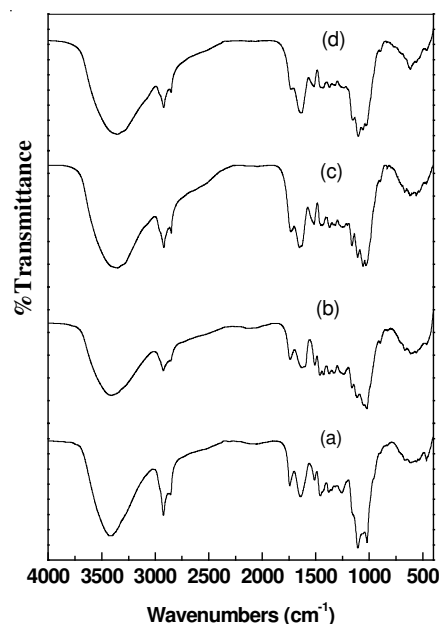

Fig. 2. FTIR spectra of combination A (a) before adsorption (b) after Ni²⁺ adsorption and (c) after Cu²⁺ adsorption (d) after Zn²⁺ adsorption

The broad and intense peak at 3500 cm⁻¹ was assigned to the presence of free or hydrogen bonded O-H groups (from carboxylic acids or alcohols) on the surface of the adsorbent[21]. The band at 2920 cm⁻¹ indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids[22]. Peak observed at 1720 cm⁻¹ is the stretching vibration of C=O functional group and may be assigned to carboxylic acids and their esters[22].

Asymmetric and symmetric stretching vibration of ionic -COO⁻, appeared at 1620 and 1500 cm⁻¹, respectively. The peaks at 1300 cm⁻¹ may be assigned to symmetric stretching of -COO of pectin[24] and aliphatic acid group vibration at 1120 cm⁻¹ to deformation vibration of C=O and stretching formation of -OH of carboxylic acids and phenols[23]. The peak at 1020 cm⁻¹ can be assigned to stretching vibration of C-OH of alcoholic groups and carboxylic acids. Hence from the FTIR study support the presence of carboxylic and hydroxyl functional group in combination A. These groups may function as proton donors, hence deprotonated hydroxyl and carbonyl groups may be involved in coordination with metal ions[25].

FTIR spectra of metals (Ni^{2+}, Cu^{2+} and Zn^{2+}) sorbed on combination A, show that the peaks expected at 3500, 2920, 1720, 1620, 1500, 1300, 1120 and 1020 cm⁻¹ had shifted, respectively to 3450, 2890, 1710, 1610, 1490, 1310, 1125 and 1015 cm⁻¹ due to Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions adsorption. These shifts in FTIR spectrum upon metal absorption support that acidic groups, *viz.*, carbonyl and hydroxyl, are primarily responsible for the metal uptake from aqueous solution[25].

Batch studies

Effect of pH on metal adsorption: The pH of the solution is one of the most important factors governing the adsorption of metal ions by the adsorbent[11]. The interaction of the different metal ions in solution with the adsorbent may be illustrated by the eqn. 5.

$$M^{n+} + AH_n \leftrightarrow AM + nH^+ \tag{5}$$
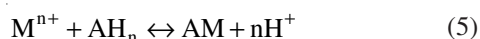
where M represent the metal, n its charge and A the active adsorption sites of the adsorbent. The competition between the metal and H^+ ions for the active sorption sites[22] on the adsorbent took place under different pH values of the solution. The pH affects both the solubility of the metal ions in the solution as well as the ionization states of the functional groups on the adsorbents. In order to study the effect of pH on metal ion adsorption on all the combination A to D, batch equilibrium studies were conducted at different pH values in the range of 2-7 for all the three metal ions as shown in Fig. 3.

The maximum biosorption of Ni^{2+}, Cu^{2+} and Zn^{2+}, by all the combinations used, were obtained at pH 6, 5 and 4, respectively and a significant decreased in biosorption capacity was observed at lower pH values. According to Low *et al.*[26] little biosorption at lower pH could be ascribed to the H^+ competing with metal ions for sorption sites. This means that at higher H^+ concentration, the biosorbent surface becomes more positively charged, thus, reducing the attraction between biosorbent and metal ions. In contrast as the pH increases, more negatively charged surface become available, thus, facilitating greater metal uptake[27]. Hence, the optimum pH for the maximum biosorption for Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions were found to be 6, 5 and 4, respectively and further column studies were carried out at the same pH.

Effect of adsorbent dose on metal adsorption: The effect of the adsorbent dose on sorption process was studied by varying the adsorbent dose in the range of 0.2-1.2 g/0.1 L with 150 mg L⁻¹ initial metal ion concentration of Ni^{2+}, Cu^{2+} and Zn^{2+}. The results are presented in Fig. 4. Increase in adsorbent dose from 0.2-1.2 g/0.1 L resulted in a rapid
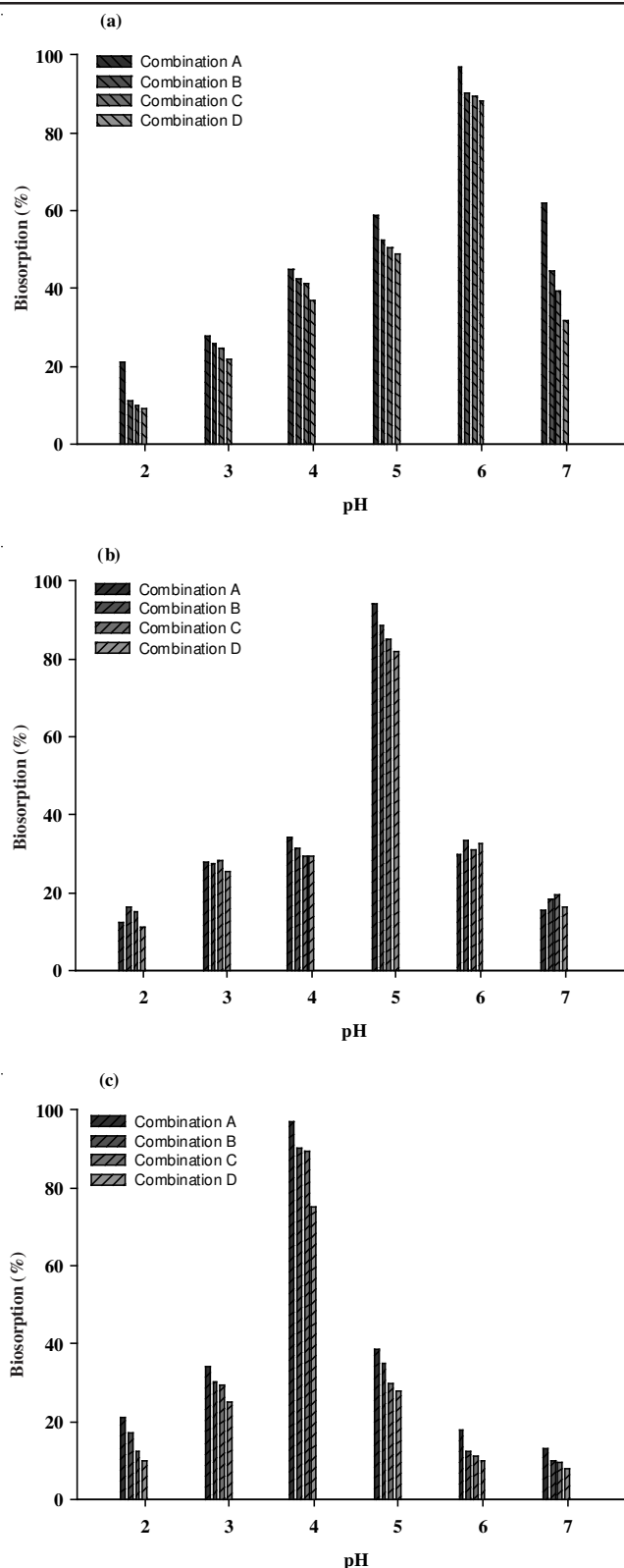

Fig. 3. Effect of pH on (a) Ni^{2+}, (b) Cu^{2+} and (c) Zn^{2+} percentage biosorption onto different combinations A to D (C_i = 150.0 mg L⁻¹, adsorbent dose = 1.0 g/0.1 L, contact time = 300 min, rpm = 225 at 30 ºC)

increase in the uptake of all the three metal ions. But no significant increase in adsorption was found beyond 1 g/0.1 L. It could be attributed to the presence of excess metal-binding sites on all the four combinations than the available Ni^{2+}, Cu^{2+} and Zn^{2+} ions in solution at the fixed concentration of 150 mg L⁻¹.
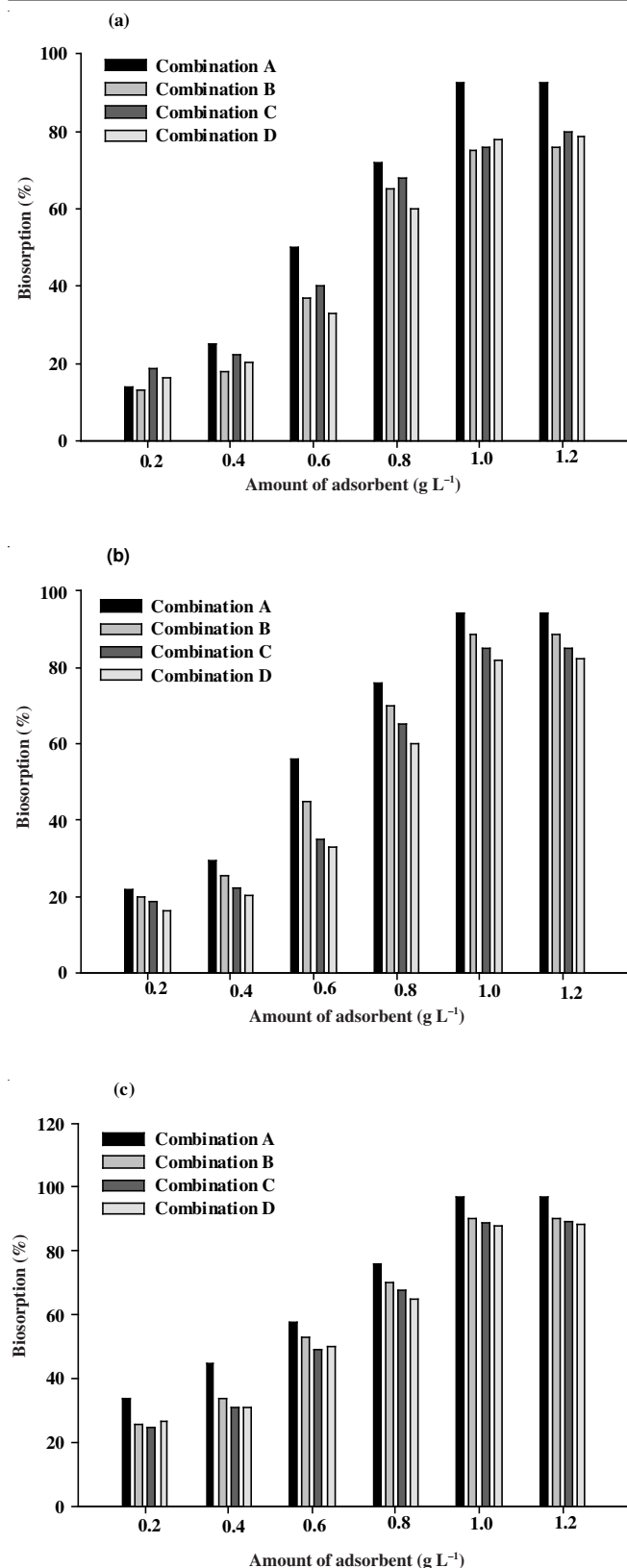
Fig. 4.   Effect of adsorbent dose on (a) Ni²⁺, (b) Cu²⁺ and (c) Zn²⁺ percentage biosorption at pH 6.0, 5.0 and 4.0, respectively onto different combinations A to D (C_i = 150.0 mg L⁻¹, contact time = 300 min, rpm = 225 at 30 ºC)

Thus 1.0 g/0.1 L was selected for further studies. These interpretations are already reported in the literature for the sorption of metals ions by different agricultural wastes[28].

Effect of contact time on metal adsorption: The effect of contact time on sorption of metal ions on different combinations were studied in the time range of 1-300 min by using 150 mgL⁻¹ of Ni²⁺, Cu²⁺ and Zn²⁺ metal ion solutions at pH 6, 5 and 4, respectively with 1 g/0.1 L of the adsorbent. The mixture was agitated at 30 ºC with 225 rpm and the samples were taken after every 20 min, filtered and analyzed by atomic absorption spectrophotometer. As shown in Fig. 5, > 70 % biosorption of all the three metal ions took place in first 1 h and then it continued to increase at a lower rate until about 92.52, 94.12 and 96.75 % biosorption was achieved for Ni²⁺, Cu²⁺ and Zn²⁺ metal ions, respectively, after 300 min of contact time. The rate of percent metal biosorption is higher in the beginning due to the availability of empty specific sites for metal ion binding. The two stage biosorption mechanism is followed, as mentioned in the literature[29] which involve a rapid biosorption for shorter duration in the first step followed by slow one for longer duration. Based on these results, a contact time of 300 min was assumed to be suitable for the subsequent biosorption experiments.

Adsorption kinetics: In order to analyze the adsorption kinetics of Ni²⁺, Cu²⁺ and Zn²⁺ by all four combinations, the pseudo-first and pseudo-second-order kinetic models were applied to the experimental data obtained. The first order rate equation of Lagergren is one of the most widely used for the sorption of a solute from liquid solution[30] and is represented by eqn. 6.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{6}$$

where q_t (mg g⁻¹) is the amount of metal ions adsorbed at time t, q_e is the amount of metal ions adsorbed at equilibrium (mg g⁻¹) and k_1 is the rate constant of the biosorption (min⁻¹).

The pseudo-first-order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites[31]. The straight line in the graph of $\ln(q_e - q_t)$ *versus* t suggests the applicability of the pseudo-first-order kinetic model. The amount of the adsorbed metal ions (q_e) and k_1 can be determined from the intercept and slope of the plot, respectively and are given in Table-3.

On the other hand, the pseudo-second-order kinetic model is based on adsorption equilibrium capacity as given in eqn. 7.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

where k_2 (g mg⁻¹ min⁻¹) is the rate constant of the second order equation; q_t (mg g⁻¹) the amount of adsorption at time t (min) and q_e is the amount of metal ions adsorbed at equilibrium (mg g⁻¹).

The plot of t/q_t *versus* t gave a straight line and the pseudo-second-order rate constant k_2 and q_e were determined from slope and intercept of the plot, respectively and are presented in Table-3.

Better fittings of the experimental values were obtained ($r^2 = 0.99$) by following the pseudo-second-order kinetic model as given in Table-3. This implies that the data confirms the pseudo second order reaction *i.e.*, the biosorption involves two phase of reaction, the first step rapid and quantitatively predominant and the second one slower and quantitatively
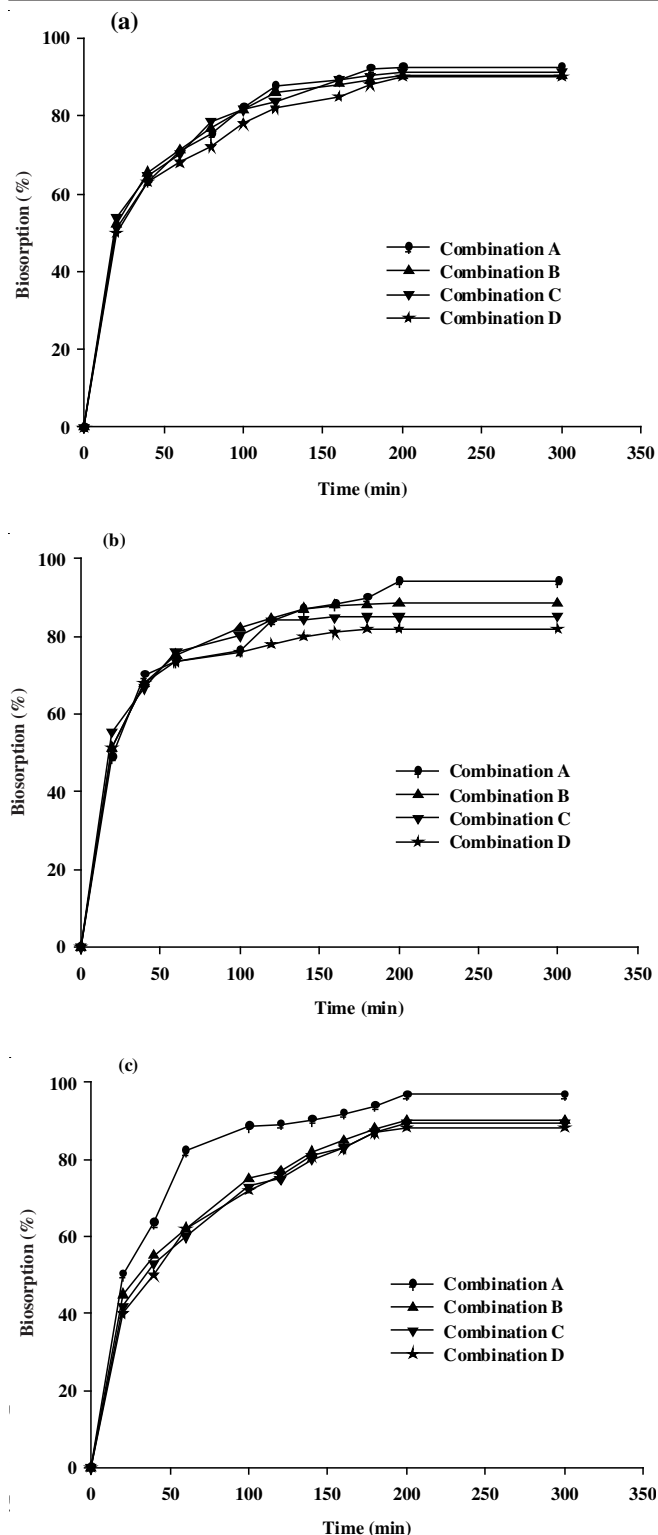
Fig. 5. Effect of contact time on on (a) Ni^{2+}, (b) Cu^{2+} and (c) Zn^{2+} percentage biosorption at pH = 6, 5 and 4, respectively onto different combinations A to D (C$_i$ = 150 mg L^{-1}, adsorbent dose = 1 g/0.1 L, rpm = 225 at 30 ºC)

TABLE-3
PSEUDO-FIRST ORDER AND SECOND-ORDER KINETIC
MODEL FOR Ni^{2+}, Cu^{2+} AND Zn^{2+} BIOSORPTION AT pH 6, 5
AND 4 RESPECTIVELY ON DIFFERENT COMBINATION A
TO D (C$_i$ = 150.0 mg L^{-1}, ADSORBENT DOSE = 1.0 g/0.1 L,
CONTACT TIME = 300 min, rpm = 225 AT 30 ºC)

Different combinations	Pseudo-first-order kinetic constants		Pseudo-second-order kinetic constants	
	k$_1$	r^2	k$_1$	r^2
Ni				
A	0.005	0.97	0.028	0.99
B	0.006	0.99	0.025	0.99
C	0.007	0.95	0.023	0.99
D	0.005	0.97	0.020	0.99
Cu				
A	0.009	0.92	0.034	0.99
B	0.005	0.92	0.027	0.99
C	0.007	0.96	0.033	0.99
D	0.006	0.94	0.033	0.99
Zn				
A	0.009	0.89	0.040	0.99
B	0.008	0.92	0.032	0.99
C	0.005	0.87	0.053	0.99
D	0.008	0.89	0.039	0.99

(A to D), were evaluated by shaking 1 g/0.1 L of the all the four combinations with varying concentrations (25-200 mg L^{-1}) of Ni^{2+}, Cu^{2+} and Zn^{2+} at pH 6, 5 and 4, respectively. Metal sorption ability all the combinations (A to D), for all three metals was found to increase with the increase in initial metal ion concentration until it reached the maximum capacity of 92.52, 94.12 and 96.75 mg g^{-1} for Ni^{2+}, Cu^{2+} and Zn^{2+}, respectively (Fig. 6).

In order to study the relationship between the metal sorption capacity (q$_e$) and the concentration of the metal ions at equilibrium (C$_e$), the adsorption equilibrium data obtained for Ni^{2+}, Cu^{2+} and Zn^{2+} were fit to Langmuir and Freundlich isotherm models. These two models are the standard models for describing equilibrium between metal ions adsorbed onto the adsorbent and metal ions remaining in solution at equilibrium at a constant temperature. The Langmuir model assumes that the uptake of the metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions and is given by eqn. 8.

$$q_{eq} = \frac{q_{max} b C_{eq}}{(1 + b C_{eq})} \tag{8}$$

where q$_{eq}$ (mg g^{-1}) is the amount of metal ions adsorbed per unit mass of adsorbent and C$_{eq}$ is the equilibrium concentration in the solution (mg L^{-1}) of Ni^{2+}, Cu^{2+} and Zn^{2+} metal ions, respectively, q$_{max}$ represents the maximum adsorption capacity (mg g^{-1}) under the experimental conditions and b is a constant related to the affinity of the binding sites (L mg^{-1}).

Freundlich derived an empirical adsorption isotherm equation, which is based on the biosorption on a heterogeneous surface and is given by eqn. 9.

$$q_{eq} = K_F C_{eq}^{1/n} \tag{9}$$

where K$_F$ and n are the Freundlich constants and are indicators of adsorption capacity and adsorption intensity, respectively.

insignificant. It has been reported that the fast reaction is due to chemisorptions[32] involving valence forces through sharing or exchange of electrons between sorbent and sorbate and slow one is by diffusion of ions into cell structure.

Metal sorption capacity and isotherm modeling: The maximum metal adsorption capacity of all the combinations
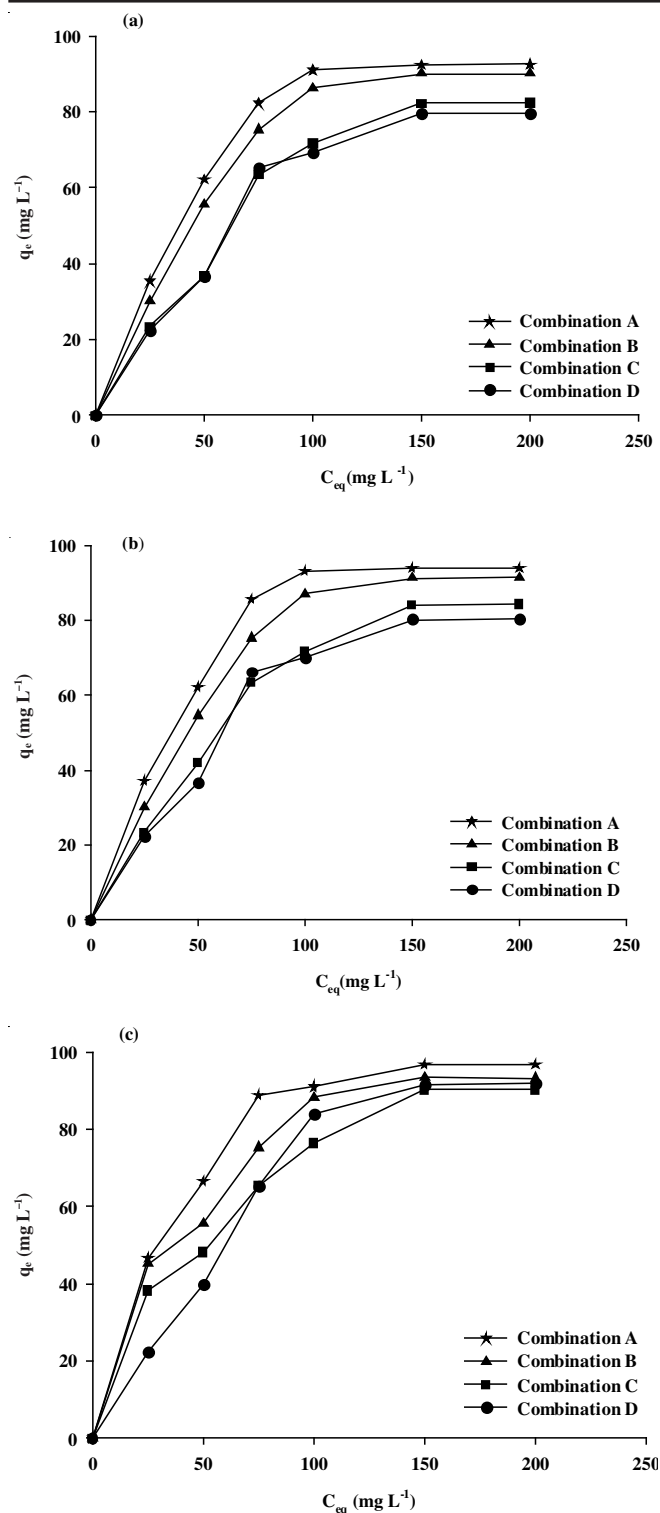
Fig. 6. Effect of initial metal ion concentration on (a) Ni^{2+}, (b) Cu^{2+} and (c) Zn^{2+} percentage biosorption at pH 6, 5 and 4, respectively onto different combinations A to D (adsorbent dose = 1 g/0.1 L, contact time = 300 min, rpm = 225 at 30 ºC)

TABLE-4
LANGMUIR AND FREUNDLICH ISOTHERM CONSTANTS
AND CORRELATION COEFFICIENTS FOR THE BIOSORPTION
OF Ni²⁺, Cu²⁺ and Zn²⁺ AT pH 6, 5 AND 4 RESPECTIVELY
ON DIFFERENT COMBINATION A TO D (ADSORBENT
DOSE = 1.0 g/0.1 L, Cᵢ = 25-200 mg L⁻¹, CONTACT
TIME = 300 min, rpm = 225 AT 30 ºC)

Different combinations	Langmuir			Freundlich		
	q_{max}	B	r^2	n	K_F	r^2
Ni						
A	90.18	0.13	0.99	2.54	0.59	0.98
B	90.10	0.11	0.99	2.19	0.41	0.98
C	89.41	0.14	0.99	2.39	0.51	0.99
D	87.13	0.17	0.98	2.66	0.77	0.93
Cu						
A	93.25	0.09	0.99	2.18	0.37	0.97
B	88.84	0.13	0.99	2.39	0.54	0.96
C	89.01	0.14	0.99	2.43	0.61	0.96
D	87.94	0.10	0.99	2.28	0.40	0.94
Zn						
A	94.87	0.12	0.99	2.26	0.50	0.99
B	90.40	0.39	0.96	4.04	1.18	0.97
C	91.80	0.10	0.99	2.22	0.35	0.97
D	88.98	0.12	0.99	2.33	0.48	0.97

which are a measure of how well the theoretical values match with the experimental data.

The theoretical maximum adsorption capacity (q_{max}) of Ni²⁺, Cu²⁺ and Zn²⁺ was calculated as 90.18, 93.25 and 94.87 mg g⁻¹, respectively. It was maximum and was given by combination A, proving it to be the best combination for desalinating mutimetal ion solutions. The theoretical value of q_{max} was quite close to the value found experimentally 92.52, 94.12 and 96.75 mg g⁻¹ for Ni²⁺, Cu²⁺ and Zn²⁺, respectively. The maximum metal uptake capacity of combination A for Ni²⁺, Cu²⁺ and Zn²⁺ was significantly higher than the metal sorption capacity of other agricultural residues reported in the literature[6-7,12-13]. Further the values of 1/n were smaller than 1 indicating that the adsorption process was favorable under studied conditions.

Total cationic contents of the combination A: Among the four combinations used, the combination A showed maximum removal for all three metal ions. For this reason it was further used to study the total cationic content release. Combination A, 1 g, was treated with 100 mL, 0.1 M HCl solution in consecutively three wash and with deionized water as control. As given in Table-5 the total amount of cations released by the combination A was 84.55 mg g⁻¹ which comprised of 12.50 20.26, 39.10 and 12.69 mg g⁻¹ of and Na⁺, K⁺, Ca²⁺ and Mg²⁺, respectively. The total amount of cations released can gives an idea about the approximate cation exchange capacity of combination A.

Adsorption mechanism: Identifying the mechanism involved in metal sorption process by the adsorbent is the real challenge in the field of metal sorption studies. Among the different mechanisms proposed in the literature[33], the ion exchange process has also been suggested to be involved in sorption process. Exchange occurs between light metal ions and protons present on the biomass and heavy metal ions present in aqueous solution[33] as shown in Fig. 7.

The Langmuir and Freundlich constants and their correlation coefficients (r^2) evaluated from these isotherms for Ni²⁺, Cu²⁺ and Zn²⁺ are given in Table-4. The sorption characteristics of Ni²⁺, Cu²⁺ and Zn²⁺ on all the combinations followed more closely the Langmuir isotherm model than the Freundlich isotherm model. This observation is further supported by the assessment of the respective correlation coefficients values

TABLE-5
MAJOR CATIONS RELEASED BY 1 g OF COMBINATION A ON ACIDIFICATION WITH 0.1 M HCl

| Wash medium/number of washings	Cations released (mg g^{-1})				
	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Total cations released
Washing with 0.1 M HCl (100 mL/wash)					
First	12.50	19.24	13.62	38.58	83.94
Second	3.24	6.11	4.34	8.12	21.81
Third	0.0	0.0	1.5	2.45	3.95
Sum of three washings (a)	15.74	25.35	19.46	49.15	109.7
Washing with deionized water (100 mL/wash)					
First	3.24	3.21	4.62	5.34	16.41
Second	0.0	1.88	2.15	3.21	7.24
Third	0.0	0.0	0.0	1.50	1.50
Sum of three washings (b)	3.24	5.09	6.77	10.05	25.15
Total cations released on acidification (a-b)	12.50	20.26	12.69	39.10	84.55
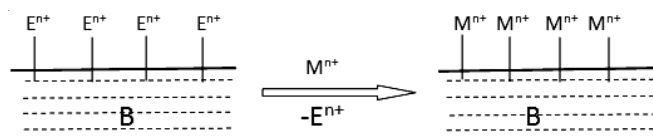
Fig. 7. The ion exchange mechanism between the exchangeable ions and the metal ions present in the solution (B = biomolecules in the biomass used, E^{n+} = Exchangeable ions (Na$^+$, K$^+$, Mg^{2+}, Ca^{2+}, H$^+$), M^{n+} = Ni^{2+}, Cu^{2+} and Zn^{2+})

In order to identify the mechanism involved in the sorption of Ni^{2+}, Cu^{2+} and Zn^{2+} onto different combination used, 1 g of the combination A was mixed with 100 mL of Ni^{2+}, Cu^{2+} and Zn^{2+} solution in three different flasks with 150 mg L^{-1} initial concentration at pH 6, 5 and 4, respectively. The mixtures so obtained were agitated in orbital shaker at 225 rpm speed for 300 min. After 300 min the mixtures were centrifuged at 5000 rpm for 10 min and analyzed for the release of Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} and unabsorbed metal ion in the solution. The results given in Table-6 supported that *ca.* 93 % Ni^{2+} removal is due to the ion exchange process involving Na$^+$, K$^+$, Ca^{2+} and Mg^{2+}. The remaining 7 % Ni^{2+} adsorption could be due to its ion exchange with protons, as pH of the supernatant was found to decrease at equilibrium. Similarly, *ca.* 93.48 and 95.20 % removal for Cu^{2+} and Zn^{2+}, respectively, was due to ion exchange with Na$^+$, K$^+$, Ca^{2+} and Mg^{2+} and the rest 6.52 and 4.96 % may be due to proton release.

Hence, it may be concluded that the sorption process for Ni^{2+}, Cu^{2+} and Zn^{2+} on combination A occurs primarily through ion exchange mechanism involving the replacement of alkali and alkaline earth metals. The protons bound to native carboxylate groups[34] are also involved in ion exchange process but to the lesser extent. Similar type of ion exchange mechanism has also been reported and dicussed for other agrowaste materials[35].

Blocking of functional groups and computation of their role in metal sorption: In order to confirm and compute the role of carboxyl and hydroxyl groups in the removal of Ni^{2+}, Cu^{2+} and Zn^{2+}, both the groups of the combination A were individually blocked in two separate experiments[18] and the results obtained after blocking them are mentioned (Table-7).

It was observed that the removal capacity of metal was badly inhibited when carbonyl groups were blocked and a decrease of 74.7, 71.7 and 70.9 % in the adsorption of Ni^{2+}, Cu^{2+} and Zn^{2+}, respectively, was observed. It clearly indicates that the carboxyl groups have the major role in the process of adsorption. On the other hand 25.3, 28.3 and 29.1 % of Ni^{2+}, Cu^{2+} and Zn^{2+} were removed by combination A, even after the blockage of carboxyl groups, indicating that other functional groups are also involved in adsorption of metal ions. To support the presence of other functional groups on the adsorbent, sorption of Ni^{2+}, Cu^{2+} and Zn^{2+} by combination A was carried out after blocking the hydroxyl groups. The adsorption capacity

TABLE-6
RELEASE OF Na$^+$, K$^+$, Mg^{2+}, Ca^{2+} AND H$^+$ AFTER SORPTION OF Ni^{2+}, Cu^{2+} AND Zn^{2+} BY THE COMBINATION A
(ADSORBENT DOSE = 1.0 g, C$_i$ = 150 mg L^{-1} for Ni^{2+}, Cu^{2+} AND Zn^{2+}, CONTACT TIME = 300 min, AT 225 rpm)

Metal ions	Total metal sorbed (mg g^{-1})	Total cations and protons released in mg g^{-1} (%)				
		Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	H$^+$
Ni^{2+}	92.52	13.5 (14.6)	19.2 (20.8)	14.6 (15.8)	38.5 (41.7)	6.6 (7.2)
Cu^{2+}	94.12	10.2 (10.7)	22.4 (23.8)	18.2 (19.3)	37.1 (39.4)	6.1 (6.5)
Zn^{2+}	96.75	12.6 (13.0)	23.0 (23.8)	17.5 (18.1)	38.9 (40.2)	4.8 (5.0)

TABLE-7
ADSORPTION OF Ni^{2+}, Cu^{2+} AND Zn^{2+} WITH AND WITHOUT BLOCKED FUNCTIONAL GROUPS ON THE COMBINATION
A (ADSORBENT DOSE = 1.0 g, C$_i$ = 150 mg L^{-1} FOR Ni^{2+}, Cu^{2+} AND Zn^{2+}, CONTACT TIME = 300 min, AT 225 rpm)

Metal ion	Adsorption on unblocked combination A (mg g^{-1})	Adsorption on carboxyl groups blocked combination A mg g^{-1} (%)	Decrease in metal sorption (%)	Adsorption on hydroxyl groups blocked combination A mg g^{-1} (%)	Decrease in metal sorption (%)
Ni^{2+}	92.52	23.42 (25.3)	74.7	63.92 (73.2)	26.8
Cu^{2+}	94.12	26.60 (28.3)	71.7	66.58 (70.7)	29.3
Zn^{2+}	96.75	28.12 (29.1)	70.9	69.00 (71.3)	28.7

of the hydroxyl group blocked adsorbent A, was found to decrease 26.8, 29.3 and 28.7 % for the removal of Ni^{2+}, Cu^{2+} and Zn^{2+}, respectively. Further, the total metal uptake capacity of carboxylic and hydroxyl group blocked adsorbent together was found to be almost equal to the total metal ions uptake by unblocked adsorbent as shown in Table-7. These results along with the functional groups study of adsorbent by the FTIR technique (Fig. 2), support that carboxyl and hydroxyl groups are mainly responsible for uptake of Ni^{2+}, Cu^{2+} and Zn^{2+} by combination A.

Column studies: The potential shown by combination A (among the four combination studied) for the removal Ni^{2+}, Cu^{2+} and Zn^{2+} in the batch studies were further tested in fixed bed column operations using electroplating industrial waste-water for the removal of the same metal ions. The data obtained in fixed bed column studies were analyzed by Thomas model as it is one of the most general and widely used models to explain the column performance theory[36]. The expression by Thomas, for the adsorption by column is given as follows:

$$\frac{C_e}{C_i} = \frac{1}{1 + \exp\left(\dfrac{k_{TH}q_e s}{R} - k_{TH}C_i t\right)} \quad (10)$$

where k_{TH} is the Thomas rate constant (mL min⁻¹ mg⁻¹), q_e the maximum metal uptake per gram of the adsorbent (mg g⁻¹), s the amount of adsorbent in gram in the column, C_i and C_e are the influent and the effluent concentrations (mg L⁻¹) of the metal ions, respectively at time t (min), $t = V_{eff}/R$ where V_{eff} is the effluent volume (mL) and R is the flow rate (mL min⁻¹).

The value of k_{TH} and q_e were determined from the plot of C_e/C_i against time t (Fig. 8) using non-linear regression analysis. The value of the regression coefficient ($r^2 > 0.99$) as given in Table-8, indicates that the model describes the column performance data very well for the biosorption of for Ni^{2+}, Cu^{2+} and Zn^{2+} in all three sorption desorption cycles in column 1, 2 and 3, respectively. It was also found that the experimental and model predicted normalized values at experimental conditions were very close. Further the metal uptake capacity found to decrease in the successive cycles in all three columns whereas Thomas rate constant did not change significantly. This behaviour was primarily attributed to gradual deterioration and depletion of binding sites caused by the acidic elution[37,38] and continuous usage or it might be due to blocking of the active sites for solute uptake by the organic moieties present in the
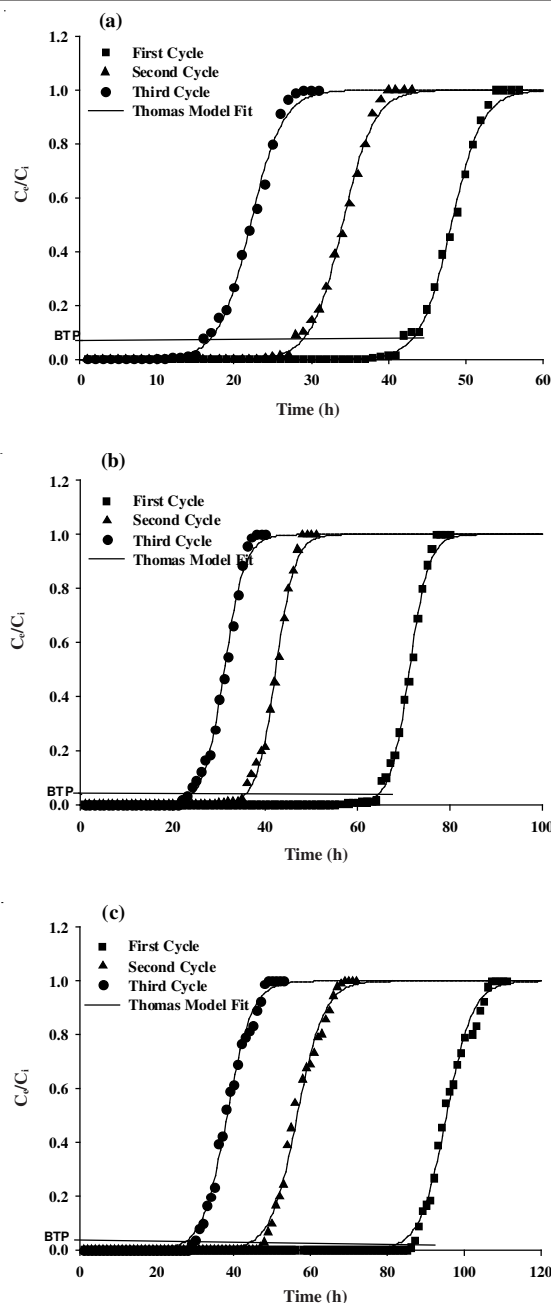

Fig. 8.   Breakthrough curves for (a) Ni^{2+} (b) Cu^{2+} and (c) Zn^{2+} during three sorption desorption cycles at pH 6, 5 and 4, respectively with electroplating effluent on combination A (adsorbent dose (s) = 10 g and flow rate (R) = 2.5 mL min⁻¹)

TABLE-8
THOMAS MODEL PARAMETERS CALCULATED CONSTANTS FOR THE Ni²⁺, Cu²⁺ AND Zn²⁺ METAL IONS
DURING SORPTION DESORPTION CYCLES WITH ELECTROPLATING EFFLUENTS ON COMBINATION A
(ADSORBENT DOSE (S) = 10.0 g, FLOW RATE (R) = 2.5 mL min⁻¹)

Cycles	Columns	k_{Th} (mL min⁻¹ mg)	q_e (mg g⁻¹)	r^2	Removal (%)		
					Ni²⁺	Cu²⁺	Zn²⁺
Column 1 (influent pH = 6.0)	1ˢᵗ Cycle	0.0041	157.40	0.99	100.0	26.0	32.0
	2ⁿᵈ Cycle	0.0041	122.25	0.99	89.3	19.7	16.6
	3ʳᵈ Cycle	0.0040	98.45	0.99	78.6	13.2	10.1
Column 2 (influent pH = 5.0)	1ˢᵗ Cycle	0.0035	124.25	0.99	0.0	100.0	25.0
	2ⁿᵈ Cycle	0.0036	88.65	0.99	18.5	88.4	13.2
	3ʳᵈ Cycle	0.0033	96.45	0.99	16.5	77.8	6.5
Column 3 (influent pH = 4.0)	1ˢᵗ Cycle	0.0028	101.55	0.99	0.0	0.0	100.0
	2ⁿᵈ Cycle	0.0027	99.56	0.99	10.8	6.5	86.5
	3ʳᵈ Cycle	0.0030	80.22	0.99	2.8	3.4	76.2

electroplating effluents[39]. The effluents from the first cycle in all three columns showed complete biosorption of Ni^{2+} in column 1, Cu^{2+} in column 2 and Zn^{2+} in column 3 satisfying the Central Pollution Control Board standards and making that water fit for reuse.

Column regeneration: The columns were regenerated thrice using 1 L of 0.1 M HCl. It can be seen form Fig. 8, the breakthrough points (BTP) was achieved earlier in second and third cycles as compared to the first cycle in all the three columns used and recharged. This may be again due to the fact that the biosorbent started deteriorating in the second and third cycle and may be also due to depletion of binding sites caused by the acidic elution[37-39] as mentioned above.

Conclusion

The present study reports the application of four different combinations, prepared by mixing various amounts of *Trifolium alexandrinum* biomass powder, *Arachis hypogea* shell powder and *Eucalyptus cameldulensis* saw dust for the removal of Ni^{2+}, Cu^{2+} and Zn^{2+} from aqueous solutions. The main aspects examined for the purpose included adsorption kinetics, isotherms modeling, FTIR spectral analysis, chemical blocking of the functional groups and the discharge of Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+ by the adsorbent during the sorption of Ni^{2+}, Cu^{2+} and Zn^{2+}. The adsorption process was found to be a function of pH, adsorbent dose, initial metal ion concentration and contact time. The adsorption kinetics was found to follow pseudo-second order kinetic model and the equilibrium sorption data was satisfactorily fitted to Langmuir adsorption isotherms. FTIR spectra analysis showed that the carboxyl and hydroxyl groups were the principal functional groups responsible for sorption of metal ions. The chemical blocking of the carboxyl and hydroxyl groups verified their participation in the metal sorption process. Further the discharge of nearly equal amount of Na^+, K^+, Ca^{2+}, Mg^{2+} and H^+ during the uptake of Ni^{2+}, Cu^{2+} and Zn^{2+} ions showed that the adsorption process was entirely ion exchange. The column studies were carried out for treating electroplating wastewater at fixed bed depth of 12.0 cm in three different columns for Ni^{2+}, Cu^{2+} and Zn^{2+} ions. Thomas model was applied to the data obtained and the breakthrough points were studied at which the columns were recharged using 0.1 M HCl. The reusability of desorbed-adsorbent in columns were tested thrice in sorption-desorption cycles, showing more than 75 % adsorption in the third cycle. Form the present study it can be concluded that the agricultural residues used in combinations are quite effective for removing different metal ions from the synthetic and industrial wastewater in batch as well as in column studies.

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