Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Preparation and Characterization of Charred Xanthated Sugarcane Bagasse for the Separation of Heavy Metals From Aqueous Solutions

Puspa Lal Homagai[a]; Kedar Nath Ghimire[a]; Katsutoshi Inoue[b]
[a] Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal [b] Department of Applied Chemistry, Saga University, Saga, Japan

To cite this Article Homagai, Puspa Lal , Ghimire, Kedar Nath and Inoue, Katsutoshi(2011) 'Preparation and Characterization of Charred Xanthated Sugarcane Bagasse for the Separation of Heavy Metals From Aqueous Solutions', Separation Science and Technology, 46: 2, 330 — 339

To link to this Article: DOI: 10.1080/01496395.2010.506903

URL: http://dx.doi.org/10.1080/01496395.2010.506903

Separation Science and Technology, 46: 330–339, 2011
Copyright © Taylor & Francis Group, LLC
ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496395.2010.506903

Taylor & Francis
Taylor & Francis Group

Preparation and Characterization of Charred Xanthated Sugarcane Bagasse for the Separation of Heavy Metals From Aqueous Solutions

Puspa Lal Homagai,[1] Kedar Nath Ghimire,[1] and Katsutoshi Inoue[2]
[1]*Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal*
[2]*Department of Applied Chemistry, Saga University, Saga, Japan*

Introduction of xanthate group onto sugarcane (Saccharum officinarum) bagasse has been investigated for the removal of cadmium, lead, nickel, zinc, and copper from their aqueous media. The charred xanthated sugarcane bagasse (CXSB) was found to have significant adsorption capacity which is more than that of various bio-sorbents mentioned in the available literatures. The newly developed bio-sorbent was characterized by SEM, FTIR, TGA/DTA, and elemental analysis. The velocity of sorption of the tested metals was fast, reaching equilibrium within 40 min. The maximum loading capacities was found to be 225 for Cd(II), 318 for Pb(II), 144 for Ni(II), 164 for Zn(II), and 178 for Cu(II) mg g^{-1}, respectively. The fast kinetics results and high adsorption capacity indicated that CXSB can be applied as the selective adsorbent for the treatment of heavy metal ions from aqueous solutions.

Keywords adsorption; charred sugarcane bagasse; heavy metals; isotherm; xanthation

INTRODUCTION

It is a matter of global concern these days regarding the heavy metal pollution into the environment due to various human activities and rapid industrialization. Cadmium, lead, mercury, nickel, zinc, copper, and chromium are often detected in appreciable amounts in industrial wastewaters, which originate from mining activities, metal plating, smelting, paint manufacture, pigment manufacture, pesticides, tanneries, printing, and photographic industries, etc. (1). Since heavy metals are non-biodegradable and can be accumulated in living tissues causing various diseases and disorders, they must be removed from solution prior to their discharge. To date, various methods including chemical treatment with lime, precipitation, ion-exchange, reverse osmosis, electro-dialysis, membrane filtration, solvent extraction, and adsorption are often used for the removal and recovery of heavy metals from wastewaters. Among them, adsorption is the most effective and widely used method for the removal of different pollutants (2). Until now, the majority of heavy metals in wastewater are removed by calcium hydroxide, in which large amounts of nontoxic metal compounds such as calcium sulfate are also precipitated together with heavy metals as a precipitated sludge, which are dumped in landfill sites. It has become difficult not only to meet stringent environmental regulation by means of the precipitation technique but there will be a problem of leakage of heavy metals back to the environment from the dumped polluted sludge. Several studies on metal removal by modified and unmodified agricultural wastes have been reported in various literatures. Recently, much attention is given to prepare adsorbents from various wastes generated from forestry (3), fishery (4,5), and by-products of agriculture (6–12). Sugarcane industries produce a large amount of sugarcane bagasse (SB) which is burnt only to produce energy for sugar mills. Since SB is a locally available industrial byproduct that requires little processing to increase its sorptive capacity, hence its cost is supposed to be low even after chemical modification. The SB contains cellulose (46.0%), hemicellulose (24.5%), lignin (19.95%), fat and waxes (3.5%), ash (2.4%), silica (2.0%), and other elements (1.7%) (13).The presence of these three main biological polymers causes sugarcane bagasse rich in hydroxyl and phenolic groups and these can be modified chemically to produce adsorbent materials with new properties (14,15). Although there are some reports of raw sugarcane bagasse as the adsorbent (16), however, owing to its low adsorption capacity, we have explored a simple means of chemical modification to enhance its metal adsorption properties in our previous study. In this study, we have further optimized the modification process and it revealed from SEM and TG/DTA studies that the present materials are better modified with the xanthate group. The choice of the xanthate group is due to the presence of sulfur atom and it is well known that sulfur group has a very strong affinity for most of the heavy metals, and the metal sulfur complex

---

Received 1 March 2010; accepted 5 July 2010.

Address correspondence to Kedar Nath Ghimire, Central Department of Chemistry, Kirtipur, Kathmandu, Nepal. Tel.: 77-1-4333945, 977-9841830466. E-mail: knghimire@yahoo.com

is very stable in basic medium (17–21). Some of the advantages of using plant wastes for wastewater treatment include a simple technique, requires little processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability, and easy generation. However, the application of raw plant wastes as adsorbents can create a lot of problems such as low adsorption capacity, Chemical Oxygen Demand (COD), and Biochemical Oxygen Demand (BOD), as well as total organic carbon (TOC) due to the release of soluble organic compounds contained in the plant materials (22). The increase of the COD, BOD, and TOC can cause depletion of oxygen content in water and can threaten life. Therefore, plant wastes need to be modified chemically before being applied for the removal of heavy metals.

The objective of the present work is to introduce a xanthate functional group onto the cellulosic network contained in sugarcane bagasse. The xanthate group containing sulphur atom has a greater tendency to form stable complexes with heavy metals ions for the separation of metals from aqueous solutions. Since the main component of the adorbents CXSB is natural polysaccharides, it is easy to be incinerated in contrast to the chelating ion exchange resins made of plastic materials. Furthermore, a comparison of chemically modified and unmodified adsorbents prepared from agricultural wastes in terms of adsorption capacity (Table 3) has been highlighted.

MATERIALS AND METHOD

Chemicals

All reagents and chemicals used in this study were of AR grade and were purchased from Wako Pure Chemical Industries, Ltd., Japan. The stock solutions (1000 mg/L) of cadmium, lead, nickel, zinc, and copper were prepared appropriately in double-distilled water from their nitrate and chloride salts, respectively. The pH of experimental solutions was adjusted by contacting with hydrochloric acid and sodium hydroxide. In all experiments a 0.1 M solution of 2-[4-(2- Hydroxymethyl)-1-piperazinyl] ethanesulfonic acid (HEPES) was used as a buffering agent purchased from Sigma Aldrich. All the working solutions of desired concentrations were diluted using either 0.1 M HCl or 0.1 M HNO_3. In all experimental work, double-distilled water was used.

Preparation of Charred Xanthated Sugarcane Bagasse (CXSB)

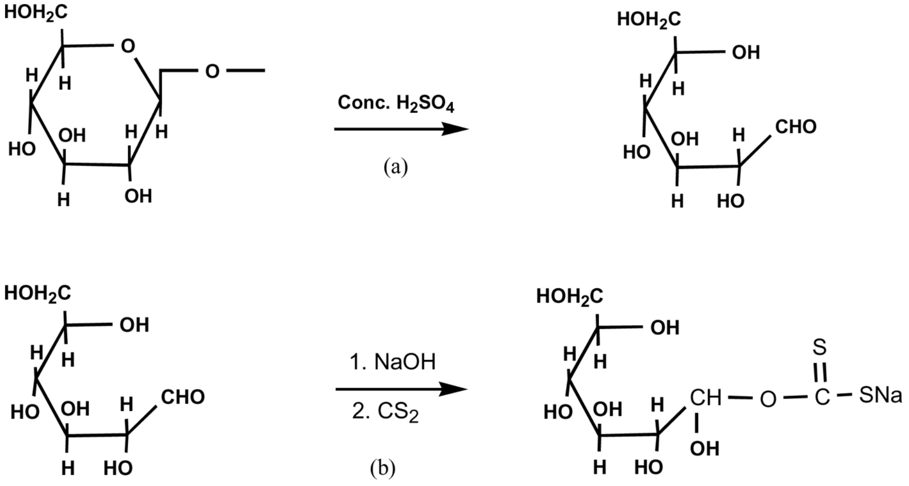
The charred sugarcane bagasse (CXSB) was prepared by washing with propanol before and after charring. The rest of the preparation process was followed in accordance with the previous article (23). It is well known that acid treatment with such biopolymer creates a suitable environment for its ring opening (24). It was washed with de-ionized water to remove excess acid and any other soluble substances until neutrality and then dried. This material is referred to as charred sugarcane bagasse (CSB). Charring is a pretreatment process, which can extract soluble organic compounds and enhance the chelating efficiency. In addition to the dehydrating property of concentrated sulphuric acid, such materials were found to be effective for further chemical modifications. In this regard, the charred material was subjected to xanthation. Fifty gm of the CSB was added into 250 ml of 15% NaOH solution and shaken for 1 h. Further, 25 ml of CS_2 was added and stirred for 3 h, then left for overnight. It was filtered and washed repeatedly until the pH of the suspension became neutral. Then the material was kept in an oven at 70°C to make it completely dry and finally it was put in desiccators. This material is ready for the experiments and called as charred xanthated sugarcane bagasse (CXSB) which is shown below in Schemes 1a,b.

Effect of pH on Metals Removal

The removal of metal ions from aqueous solution by adsorbent is dependent on the pH of the solution, as the latter affects the surface charge of the adsorbents and the degree of ionization of the adsorbate. Batch adsorption tests for various metal ions removal were carried out to examine the adsorption behavior onto CXSB. Adsorption of metals was studied by keeping the respective metal ions concentration constant (50 mg/ L) as the function of pH. All batch tests were carried out in 50 ml Erlenmeyer flasks by taking 20 mg of dried CXSB together with 15 ml of different synthetic metal ions solutions. The flasks were then agitated in a thermostated shaker maintained at 30°C and 138 rpm for 24 h to attain equilibrium. After 24 h, the suspensions were filtered through a 1 μm filter paper and their equilibrium concentrations were measured by AAS. The adsorbed amounts of metal ions were calculated from the decrease in the metal ions concentrations.

Adsorption Experiments

The main objective of an isotherm is to evaluate the capacity of the modified biomass to sequester heavy metals from an aqueous solution. Several authors have studied adsorption data using Langmuir and Freundlich adsorption isotherms (25). The test solutions of cadmium(II), lead(II), nickel(II), zinc(II) and copper(II) were prepared from corresponding standard stock solutions by diluting with 0.1 M nitric acid and 0.1 M of HEPES as a buffering agent, respectively. The pH of the solution was maintained by adding a small amount of nitric acid or sodium hydroxide. In the batch-wise tests, 20 mg of dried adsorbent was taken into a 50 ml conical flask with 15 ml of corresponding prepared diluted metal solution. The flasks were shaken vigorously in a thermostated shaker at 303 K at 150 rpm for 24 h to ensure that the equilibrium is attained. The initial and equilibrium concentrations of the metal ions were



SCH. 1. (a) Proposed ring opening of monomeric unit of cellulose contained in sugarcane bagasse followed by (b) xanthation.

measured by using an atomic absorption spectrophotometer. The adsorption efficiency, A%, of the metal ion, was calculated from

$$A\% = \frac{C_i - C_e}{C_i} \times 100 \tag{1}$$

The sorption capacity of metal ions is the concentration of the metal ions on the adsorbent and can be calculated based on the mass balance principle where

$$q = \frac{C_i - C_e}{W} \times \frac{L}{1000} \tag{2}$$

In the above Eqs. (1) and (2), q represents the amount of metal uptaken per unit mass of the adsorbent (mg g^{-1}), L is the volume of the test solution (ml), W is the dry mass of the adsorbent (g), and C_i and C_e the initial and final concentrations (mg dm^{-3}), respectively.

Kinetic Studies

The kinetic parameters of adsorption systems, which are helpful for the prediction of the adsorption rate, give important information for designing and modeling the processes. Thus, the effects of contact time were analyzed from the kinetic point of view. Throughout the study, the kinetics of several metal ions was investigated by using 20 mg CXSB with 15 ml (100 mg L^{-1}) metal aqueous solutions into thirteen Erlenmeyer flasks of 50 ml for each metal ion separately for the provision of 5–240 min equilibration at their respective optimum pH condition.

Desorption Studies

Desorption experiments were carried out by a metal-loaded CXSB sorbent (1.0 g) with 50 ml of 0.1 M HNO_3 as the desorbing agent in 250 ml Erlenmeyer flasks and was shaken in a rotary shaker for 60 min at room temperature. The metal-loaded CXSB suspension was centrifuged and the supernatant was analyzed for the desorbed metal ions. After each cycle of adsorption-desorption, the CXSB sorbent was washed with distilled water and the regenerated CXSB was treated with 0.1 M $CaCl_2$ for 15 min, followed by washing, filtering, and drying before use in further experiments. This metal-desorbed CXSB was used as the regenerated sorbent in five repeated sorption-desorption cycles to determine the reusability potential of the adsorbent. The measurement was done at respective wavelengths of different metals with a slit width 0.7 nm using an air-acetylene flame. Experimental samples were filtered using Whatman 1-mm filter paper and the filtrates were analyzed after suitable dilutions.

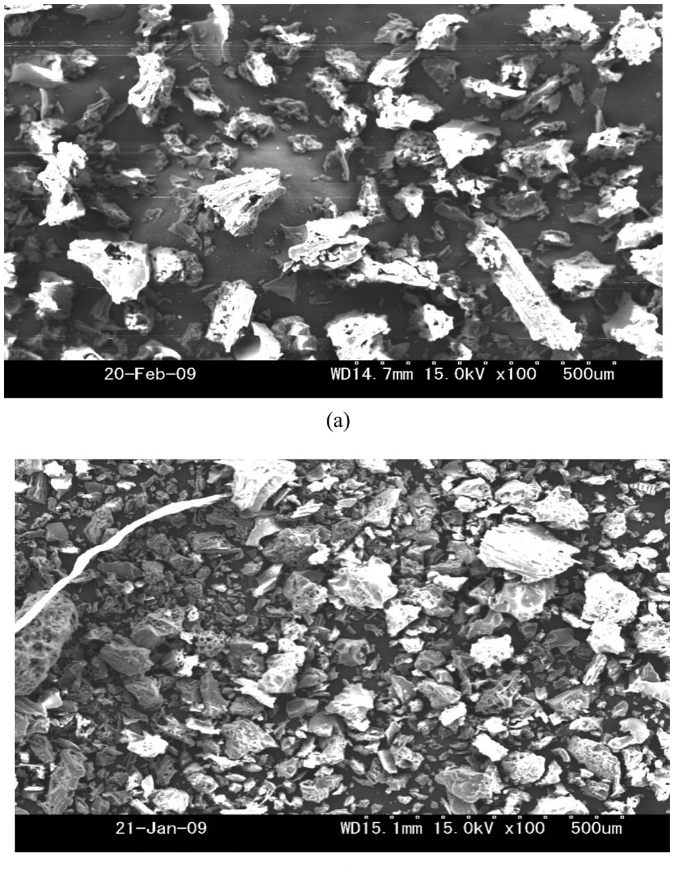
Analysis

The morphological characteristics of CSB and CXSB were visualized via scanning electron microscope (SEM) using an S-3000 N Scanning Electron Microscope of HITACHI, Japan, at 2000x magnification. The functional groups present in the adsorbent were characterized by a Fourier transform infrared (FTIR) spectrophotometer (FT/IR-410 (JASCO, Japan), using KBr discs to prepare the CSB and CXSB samples. Thermal gravimetric analysis (TGA) was carried out on a thermal analyzer (Model TG/DTA –6300, Seiko Instrument Inc. Extar) at a heating rate of 10°C per min under nitrogen atmosphere. The pH of the sample solution was measured using a pH meter, HM-30 R, TOA-DKK while the concentrations of the several metal ions were measured by using a Shimadzu AA-6650 Atomic Absorption Spectrophotometer. Standard solutions of various metal ions of 1000 mg/L were diluted to the desired concentrations and used for AAS calibration. Each of the batch tests were equilibrated by shaking in a Thermostatic Shaking Incubator AT 24 R, Japan.

RESULTS AND DISCUSSION

SEM

A Scanning Electron Microscopy (SEM) was used to observe the surface morphologies of CSB before modification and CXSB after chemical modification. The fiber surface of CSB was found to be relatively rough and non-uniform due to hydrolysis reaction on the surface of SB. The activation process of CSB by sulphuric acid treatment leads to corrosion on the surface of carbonaceous material and introduces micro-, meso-, and macro-pores after chemical modification. The surface morphology of CSB and CXSB was characterized by SEM images shown in Figs. 1a and 1b. It can be seen that the external surface of CXSB is full of cavities like a honeycomb structure. The xanthation process had considerably enhanced the morphology of charred sugarcane and its physical, chemical, and biodegradable characteristics, which varies with respect to the nature of synthetic side chains incorporated. SEM observations of CSB revealed its non-uniform and rough surface that changed into a honeycomb structure of CXSB. The CXSB showed apparently isolated and irregularly distributed pores, which are supposed to be formed due to the increase of the effective diffusion surface area derived from pore formation in the modified sugarcane bagasse.



(a)

(b)

FIG. 1. Scanning electron microscope (SEM) photographs of CSB and CXSB at 2,000x.

FTIR Spectra and Elemental Analysis

FTIR is a useful tool to identify the presence of certain functional groups in a molecule as each specific chemical bond often has a unique energy absorption band. The spectral analysis was employed to confirm changing of functional groups for pretreated and xanthated sugarcane bagasse. The FTIR spectra of the CXSB was recorded with the KBr dispersion method and shown in Fig. 2. The broad, intense absorption peaks observed at 3442 cm^{-1} are due to the existence of bounded hydroxyl groups. The peaks observed at 2930 cm^{-1} can be assigned to the C-H group, and peaks around 1042 cm^{-1} are characteristics of C-O group of primary hydroxyl stretching that may be attributed to cellulose structure of the sugarcane bagasse. The band at 1754 cm^{-1} that was observed is due to the –CHO group formed during the charring process before the modification of CSB. This peak disappears after modification of CSB into CXSB and an intense broad band depicted in Fig. 2 is observed at 1558 cm^{-1} revealing that the xanthate group has been introduced onto CSB. Absorption peaks appeared at 1558 cm^{-1} corresponding to the C = S stretching vibration of the xanthate unit and it may be attributed to the –CS$_2$H deformation suggesting that CXSB has been successfully xanthated. The stretching vibration of C = S, S = O and S-S found at 1176, 1022, and

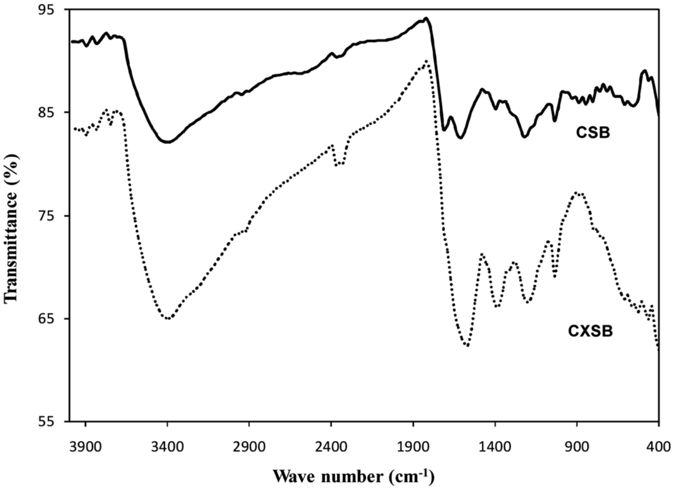


FIG. 2. FTIR of (a) CSB (before modification) and (b) CXSB (after modification).

460 cm^{-1}, respectively in the spectrum of CXSB were strongly indicative of the presence of the xanthate group bonded to the charred materials. The major absorption bands characteristic of the C = S groups lay in the region 1563–700 cm^{-1} (26). This region is much more intense for CXSB in comparison to CSB. The peak corresponding to C-S-S and C-O-C symmetric stretching seemed to have merged into a broad band at 1558 cm^{-1}. The asymmetric stretching vibration of C-O-C is observed at 1176 cm^{-1}. The very weak vibration for C-S is also observed around 605 cm^{-1}.

The amount of carbon, hydrogen, and nitrogen in raw sugarcane bagasse was found to be 46.58%, 6.11%, and 0.11% whereas after chemical modification 52.35%, 2.12%, and 0.22%, respectively for CXSB. The percentage of sulfur had been determined to be as 4.92% which confirmed the proper modification of charred sugarcane bagasse by the introduction of the xanthate group in the xanthation process.

Thermal Analysis

Thermal analysis (TG) was performed to understand the stability characteristics of the charred sugarcane bagasse (CSB) cellulose and charred xanthated sugarcane bagasse (CXSB) cellulose, which is important during the processing of fibers into composites. The experiments were carried out under continuous N_2 atmosphere using a thermal analyzer with a heating rate of 10°C min^{-1}. The charred sugarcane bagasse degraded mainly in two decomposition steps: the first at 250°C and second one at 450°C. Same way, CXSB also showed two decomposition steps at 300°C and 810°C, respectively. These results are depicted in the TGA and DTA curves shown in Fig. 3 for CSB and CXSB. The first stage started at about 100°C for all the materials with weight loss of 10–20% due to loss of physically adsorbed water on membrane surfaces. The second stage exhibited a rapid weight loss at 250–450°C and 300–810°C for CSB and CXSB, respectively. The maximum oxidation reached at 450°C for CSB and 810°C for CXSB. The second degradation stage of CXSB took place at higher temperatures than the corresponding stage of CSB indicating that CSB is less stable than CXSB. The weight loss for CSB (250–450°C) and CXSB (300–810°C) were found to be about 90% and 80%, respectively. The DTA curves revealed interesting and more accurate differences of the thermal behavior of the CSB and CXSB than the TGA curves. The DTA peak of CXSB had shown its maximum value at about 810°C, while it is 450°C for CSB indicating a strong evidence in the increase in thermal stability of the CXSB over CSB. From the aforementioned analysis it is concluded that chemical modification has taken place within the CSB.

Effect of pH on Adsorption of Various Metal Ions

The pH of a solution played an important role for the adsorption of metal ions. At low pH, there is high concentration of H^+ that has high mobility as compared to metal ions and competition between H^+ with metal ions decreases their adsorption. On the other hand, as the pH value of the solution increases, adsorption also increases due to a lesser number of H^+ and a greater number of surface ligands with negative charges. The low adsorption of metal ions at low pH may be due to sorbate lyophobic behavior (22). The same way, the solubility of metal in solution decreases with increasing pH and the sorption increases with increasing pH. The optimum pH for Cd, Pb, Ni, Zn, and Cu biosorption was found to be 5, 4, 4, 6, and 5, respectively as shown in Fig. 4. The optimum pH of the solution can be explained on the basis of pH_{pzc}

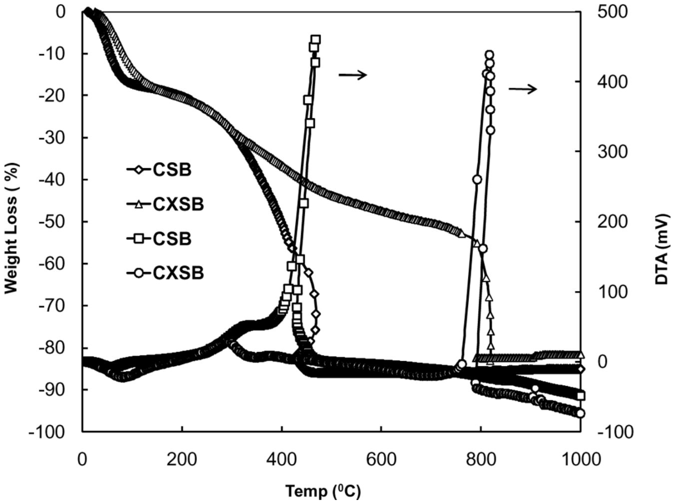


FIG. 3. TG-DTA curves of CSB (before modification) and CXSB (after modification).

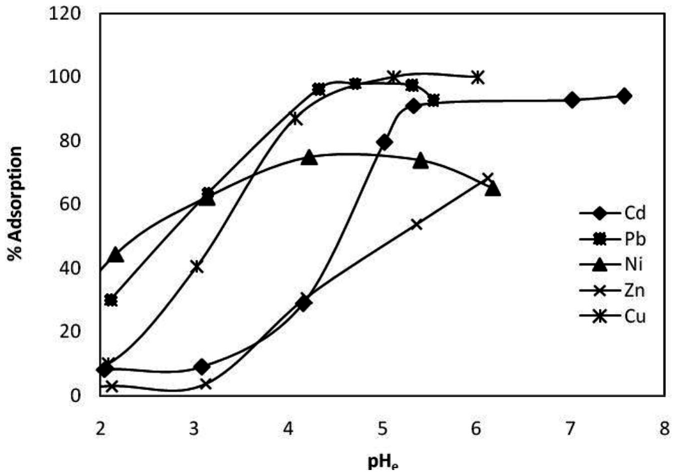


FIG. 4. Effect of pH on adsorption of Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) by CXSB.

(point of zero charge). The pH_{pzc} is the pH at which the net charge of the adsorbent surface becomes zero. The point of zero charge for CXSB was found to be 4 as shown in Fig. 5. Below pH_{pzc} ($pH < 4$) the surface charge is positive and above pH_{pzc} ($pH > 4$), the surface charge of the xanthated adsorbent is negative. Hence at more than pH 4, the sorption of the metal ions increased while the adsorption of metal ions decreases at pH less than 4. This signifies that the adsorption of metal ion takes place according to the ion exchange mechanism. The amount of adsorption above pH_{pzc} was maximum due to the interaction of metal ions (M^+) and $M(OH)^+$ with a negatively charged adsorbent surface. At low pH, particularly below pH_{pzc}, the positively charged M^+ and $M(OH)^+$ species may repel with the positively charged adsorbent surface having an identical charge and thereby decreases the metal ion adsorption. The selectivity order in the removal of heavy metals at pH around 4 follows the order Pb > Cu > Ni > Cd > Zn. Pauling electronegativity values for these atoms are 2.33, 1.90, 1.90, 1.69, and 1.65, respectively. As the electronegativity of the atom increases, their ionic form seems to be more easily sorbed by the bioadsorbent. This is in full accord with the results obtained earlier (27).

Adsorption Isotherms

The study of adsorption isotherms indicates the adsorption capacities of adsorbents at experimental condition. Isotherms help to determine the adsorptive capacity of material and further help to evaluate the mechanism of performance of the adsorption system. It is done by characterizing the equilibrium state of the functionalized adsorbent that has been allowed to react with the aqueous solution of the metal of interest. Here isotherm studies were performed using various concentrations of metal ions ranging from 25 to 1000 mg dm^{-3}. For batch adsorption experiment, 20 mg of adsorbent was equilibrated with 15 ml of corresponding synthetic metal solution in a 50 ml Erlenmeyer flask for 24 h to attain equilibrium. Sorption isotherms were evaluated using the linearized Langmuir and Freundlich model represented by Eqs. (3) and (4), respectively.

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \tag{3}$$

$$ln\, q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where q_e (mg/g) is the amount of adsorbed metal ions per gram of adsorbent; C_e (mg/L) is the residual concentration of metal ion after adsorption, q_m (mg/g) the maximum adsorption capacity, b (L/mg) the binding constant. In Eq. (4), K_F and $1/n$ are the Freundlich constants related to the adsorptive capacity and the intensity of adsorption, respectively. The Langmuir constants (q_m and b) were calculated from the plots of C_e/q_e versus C_e, and Freundlich constants (K_F and $1/n$) were obtained from $\ln q_e$ versus $\ln C_e$ plots using the above linearized equation (data not given). The Langmuir constants and its correlation coefficients evaluated from the isotherm for Cd^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} and Cu^{2+} are given in Table 2. The high value of the Langmuir correlation coefficient ($R^2 = 0.99$) confirmed that the Langmuir isotherm is best fitted than the Freundlich isotherm onto CXSB. The maximum adsorption capacity based on experimental results as shown in Fig. 6 was to be 250, 333, 167, 200, and 200 mg g^{-1}, respectively, which revealed that the active sites of the biomass CXSB are constant and independent of the metal solution used. The values of b are indicative of the affinity of the sorbent by the sorbate, and high values of b are associated with high metal adsorbed/metal desorbed ratio (28). The b constant is higher for lead than for other metals indicating that it has higher affinity towards the active sites of the adsorbent materials. Furthermore, the affinity of CXSB by the metals followed the order: $Pb^{2+} > Cd^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+}$. On

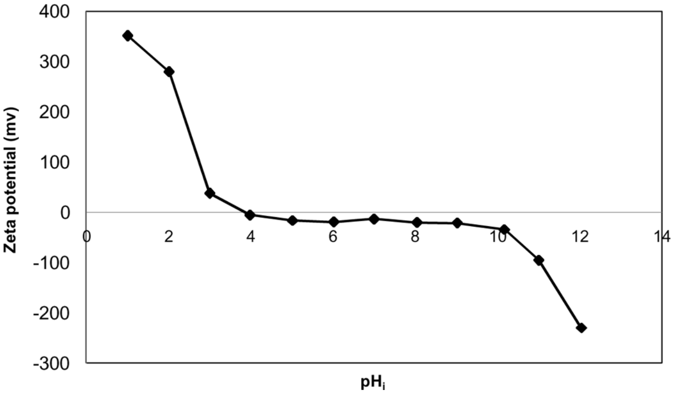


FIG. 5. Point of zero charge (pH_{pzc}) curve of CXSB.

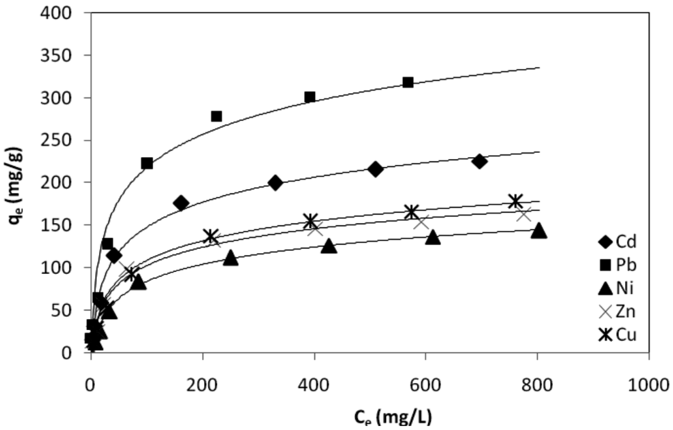


FIG. 6. Adsorption isotherm plot for the adsorption of metals ions onto CXSB.

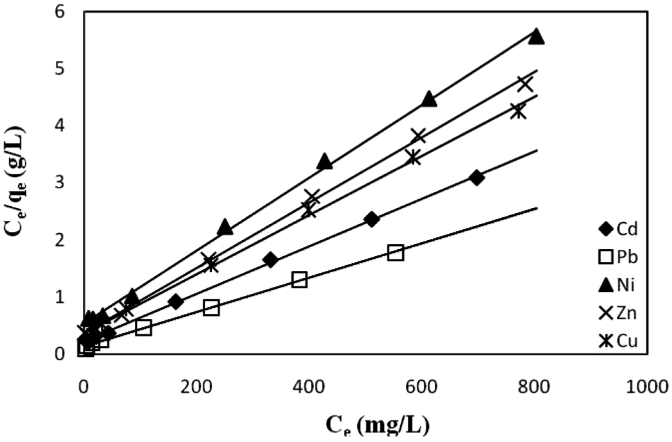


FIG. 7. Langmuir isotherm plot for the adsorption of metal ions onto CXSB.

the other hand, the theoretical monolayer capacity (q_m) of the above respective metal ions based on the Langmuir adsorption equation as shown in Fig. 7 was determined to be 225, 318, 144, 165, and 178 mg g^{-1}, respectively. These results are in close agreement against each other suggesting that heavy metals can be quantitatively sequestered onto CXSB (Table 1).

The essential characteristics of the Langmuir isotherm can be expressed by a dimensionless constant called the equilibrium parameter R_L as expressed by Eq. (5).

$$R_L = \frac{1}{1 + bC_o} \tag{5}$$

where b is the Langmuir constant and C_o is the initial metal ions concentration. R_L values represent the type of isotherm and its value between 0 and 1 indicates favorable adsorption. The R_L values evaluated (data not given) from the b values for all metal ions at various concentrations had shown that all values were found to be between 0 and 1, indicating further support for the Langmuir model (29).

TABLE 1
Langmuir adsorption isotherm model parameters and experimental q_{max}

Metal ions	q_{max} (mg/g) Langmuir model	q_{max} (mg/g) experimental	b (L/gm)	R^2
Cd(II)	225	250	0.018	0.997
Pb(II)	318	333	0.023	0.995
Ni(II)	144	167	0.011	0.996
Zn(II)	165	200	0.013	0.993
Cu(II)	178	200	0.014	0.991

TABLE 2
Sorption kinetics of pseudo second order for several metal ions onto CXSB

Metal ions	R^2	K_2 (g/mg/min)
Cd (II)	0.99	3.61×10^{-2}
Pb (II)	0.99	3.26×10^{-2}
Ni (II)	0.99	90.0×10^{-2}
Zn (II)	0.99	1.28×10^{-2}
Cu (II)	0.99	9.63×10^{-2}

Sorption Kinetics

The rate of metal sorption is an important factor and a prerequisite for the determination of a successful practical adsorption application. The sorption kinetics of the metal ions onto CXSB was analyzed as the function of time at an initial concentration of 100 mg/L solutions. The concentrations of the metal ions were analyzed keeping their optimum pH in a regular and certain interval of time by AAS. From the experimental data, it was observed that the percentage of adsorption increased with the increase in time from 5 min up to 40 min and then it became constant in the range of 15 min to 240 min as shown in Fig. 8. All the kinetic data of the respective metal ions were tested by using the pseudo-first order rate equation and was found to be of very low (data and figure not given) Lagergren correlation coefficient (R^2) value. Hence the pseudo-second order kinetics model has been used to evaluate the experimental kinetic adsorption data. Adsorption kinetics was explained by the pseudo-second order model given by Ho and Mckay (30) as follows in the integrated form:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where q_t(mg g^{-1}) is the amount of the adsorption at time t (min), K_2(g mg^{-1} min^{-1}) is the rate constant of the pseudo-second order kinetic adsorption. The values of K_2 and q_e can be obtained from the intercept and slope of the plot of the experimental t/q_t versus t. Figure 9 depicts the experimental data which can be explained by the pseudo-second order kinetic model, with the correlation coefficient R^2 being almost unity (0.99) for all the metal ions. The regression coefficient of above 0.99 shows that the model can be applied for the entire adsorption process and confirmed the chemisorption of all metal ions onto the CXSB (31). The experimental value of K_2 was found to be 3.61×10^{-2}, 3.26×10^{-2}, 90×10^{-2}, 1.28×10^{-2}, and 9.63×10^{-2} g mg^{-1} min^{-1}, respectively for the mentioned metal ions. It is well known that the higher the value of the rate constant the faster is the rate of adsorption. Hence

TABLE 3
Comparison of adsorption capacities (mg/g) of different biosorbents for the removal of various metal ions reported in the literatures

Adsorbents	Cd (II)	Pb (II)	Ni (II)	Zn (II)	Cu (II)	References
Xanthated sugarcane bagasse	225	318	144	164	178	This study
Modified sugarcane bagasse	195	188	–	–	113	(16)
Soluble starch xanthates	33	17	–	–	–	(17)
Modified sugarcane bagasse	164	313	–	–	139	(34)
Laminaria japonica	155	236	–	91	100	(11 & 35)

the rate of adsorption for the respective metal ions onto CXSB found experimentally from K_2 values are in the order: Ni(II) > Cu(II) > Cd(II) > Pb (II) > Zn (II) with the required equilibration time 15, 20, 25, 25, and 35 min, respectively. The kinetics experiment thus indicated that the CXSB adsorbent might be effective for the removal of the heavy metals from aqueous solution within 35 minutes.

Plausible Adsorption Mechanism

The probable mechanism between Metal–CXSB interaction could be electrostatic, ion exchange, and/or specific chemical reaction. The metal adsorption was found to be maximum at optimum pH of each respective metal ion and decreased in the pH range below the point of zero charge (pH_{pzc}). The adsorption sites for the aforementioned metals are at sulfur atoms attached to the xanthate groups. The xanthate groups are unprotonated above pH 1.5 and have a net negative charge and hence the adsorption of metals with CXSB started above pH 2. Since the CXSB has a very low specific surface area ($\sim 25\,m^2/g$), physical adsorption alone cannot contribute to the higher metal ion uptake capacity, so the predominant mode of adsorption is the chemisorption. The cation from the xanthate group contained in the monomeric unit has been exchanged at the cost of metal ions present in the solution. A schematic representation of the complexation mechanism of the metal ions with the xanthate group which had taken place through the ion exchange process, is shown in Scheme 2. According to the HSAB theory by Pearson, xanthate is a soft base and it tends to form stable complexes with soft acids like heavy metal ions (32). The metals such as Cd (II), Pb(II), Ni(II), Zn(II), and Cu(II) are larger and more polarizable and the ligands, charred xanthated sugarcane bagasse will have a much higher affinity towards the metal ions and the sorption capacity was found to be higher than its raw biomass. For example, the precipitate formation constant (K_s), which indicates the strength of the metal and the ligand complex, shows that the lead complex with sulfur is stronger even than the lead hydroxide complex (33); $Pb(OH)_2$ $K_s = 10^{15.2}$, $Pb(HPO_4)$ $K_s = 10^{11.36}$, PbS $K_s = 10^{27.5}$, $PbSO_4$ $K_s = 10^{8.0}$. This strong affinity between sulfur and lead may result in a high affinity constant.

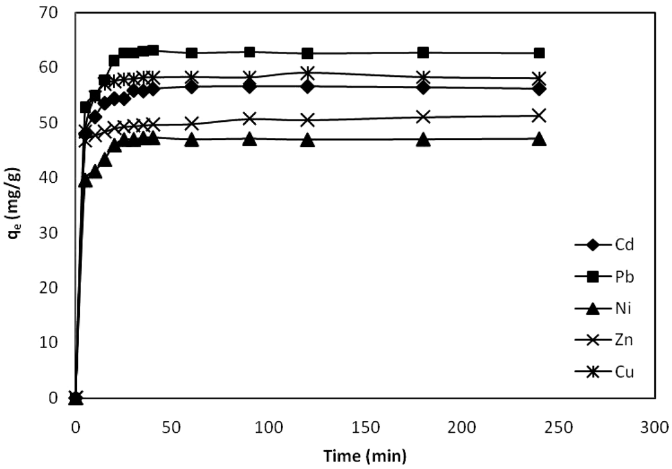


FIG. 8. Amounts of adsorption versus adsorption times for Cd(II), Pb(II), Ni(II), Zn(II) and Cu(II) onto CXSB.

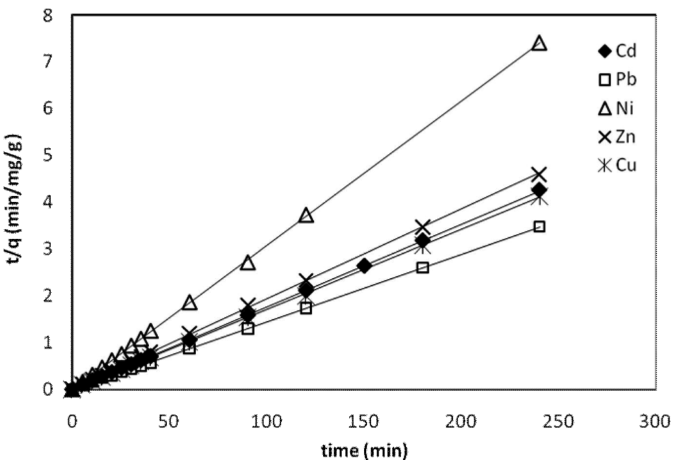
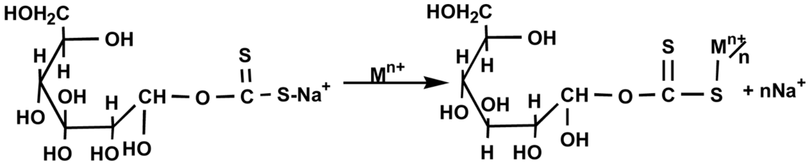


FIG. 9. Pseudo second order sorption kinetics of Cd(II), Pb(II), Ni(II), Zn(II) & Cu(II) on CXSB.



SCH. 2. Plausible adsorption mechanism of metal ion onto monomeric cellulose unit contained in CXSB.

Desorption and Recycling Studies

Desorption studies were carried out by the batch method for the evaluation of the adsorbed metals as well as the regeneration of the adsorbent. As for example, with 0.1 M HNO_3, as a eluting agent, Pb(II) desorbed from CXSB was found to be 93%. After three cycles of operation the adsorption capacity decreased from 97% to 78%. Regeneration of the charred carbon with 0.1 M $CaCl_2$ was efficient for further use. In the present study, 78% desorption was achieved for Pb^{+2} with 0.1 M HNO_3 solution. Thus the study reveals that the adsorbent can be reused which makes the process more economical and eco-friendly due to minimal solid waste generation. The regeneration and desorption aspect of the remaining metals onto CXSB needs further studies for their real cost effectiveness.

CONCLUSIONS

A specific new type of adsorbent CXSB was prepared by treating the CSB with carbon disulphide under alkaline medium. The CSB was successfully xanthated and that was confirmed by SEM, FTIR, and TG/DTA characterization. The adsorption capacity of metal ions increased with an increase of pH value up to the optimum pH of each metal ion. Adsorption studies were compared with the Langmuir and Freudlich model in which the data fitted well only the Langmuir isotherm model. The velocity of adsorption was fast and followed pseudo-second order kinetics. This signifies that the introduction of the xanthate group onto charred sugarcane bagasse is of importance in enhancing the adsorption capacities of raw sugarcane bagasse. Finally, we can conclude that chemically modified xanthated sugarcane bagasse can be used as a low cost adsorbent in the fast treatment of metal-containing effluents.

ACKNOWLEDGEMENTS

The authors would like to thank National Academic Science and Technology (NAST, Nepal) for providing partial support to carry out this research work.

REFERENCES

1. Kadirvelu, K.; Thamaraiselvi, K.; Namasivayam, C. (2001a) Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. *Bioresour. Technol.*, 76: 63.
2. Gupta, V.K.; Ali, I. (2004) Removal of lead and chromium from wastewater using bagasse fly ash – a sugar industry waste. *J. Colloid Interface Sci.*, 271: 321.
3. Horsfall Jr., M.; Abia, A.A.; Spiff, A.I. (2006) Kinetic studies on the adsorption of Cd^{+2}, Cu^{+2} and Zn^{+2} ions from aqueous solutions by cassava (Manihot sculenta Cranz) tuber bark waste. *Biores. Technol.*, 97: 283.
4. Inoue, K. (1999) Application of chitosan in separation and purification of metals. In: *Recent Advances in Marine Biotechnology*, Oxford & IBH Publishing Pvt. Ltd. pp. 63–97.
5. Ghimire, K.N.; Miyajima, T.; Yoshizuka, K.; Shoji, T. (2001) Adsorption of some metal ions and mineral acids on chitin. *Chitin and Chitosan Res.*, 7: 61.
6. Lokesh, K.S.; Tare, V. (1989) Cadmium starch- xanthate interaction in aqueous system under varied environmental conditions. *Indian Journal of Environmental Health*, 31: 145.
7. Reddad, Z.; Gerente, C.; Andres, Y.; Cloirec, P.L. (2002) Adsorption of several metal ions onto a low- cost biosorbent: kinetic and equilibrium studies. *Environ. Sci. Technol.*, 36: 2067.
8. Saeed, A.; Iqbal, M.; Aktar, M.W. (2005) Removal and recovery of heavy metals from aqueous solution using papaya wood as a new bio-sorbent. *Sep. Pure Technol.*, 45: 25.
9. Pavasant, P.; Apiratikul, R.; Sungkhum, V.; Suthiparinyanont, P.; Wattanachira, S.; Marhaba, T.F. (2006) Biosorption of Cu^{+2}, Cd^{+2}, Pb^{+2} and Zn^{+2} using marine green macroalga Caulerpa lentillifera. *Biores. Technol.*, 97: 2321.
10. Biswas, B.K.; Inoue, K.; Ghimire, K.N.; Ohta, S.; Harada Ohto, H.; Kawakita, H. (2007) The adsorption of phosphate from an aquatic environment using metal loaded orange waste. *J. Colloid Interface Sci.*, 312: 214.
11. Ghimire, K.N.; Inoue, K.; Ohto, K.; Hayashida, T. (2008) Adsorption study of metal ions onto crosslinked seaweed Laminaria japonica. *Biores. Technol.*, 97: 32.
12. Dakal, R.P.; Ghimire, K.N.; Inoue, K. (2005) Adsorptive separation of heavy metals from an aquatic environment using orange waste. *Hydrometallurgy*, 79: 182.
13. Sene, L.; Converti, A.; Felipi, M.G.A.; Zilli, M. (2002) Sugarcane bagasse as alternative packing material for bio-filtration of benzene polluted gaseous streams: A preliminary study. *Biores. Technol.*, 83: 153.
14. Xiao, B.; Sun, X.F.; Sun, R. (2001) The chemical modification of lignins with succinic anhydride in aqueous systems. *Polymer Degradation and Stability*, 71: 223.
15. Navarro, R.R.; Sump, K.; Fujii, N.; Matsumura, M. (1996) Mercury removal from wastewater using porous cellulose carrier modified with polyethyleneimine. *Water Research*, 30 (10): 2488.
16. Gurgel, L.V.A.; Freitas, R.P.; Gil, L.F. (2008) Adsorption of Cu(II), Cd(II), and Pb(II) from aqueous single metal solutions by sugarcane bagasse and mercerized sugarcane bagasse chemically modified with succinic anhydride. *Carbohydrate Polymers*, 74: 922.
17. Tare, V.; Chaudhari, S. (1987) Evaluation of soluble and insoluble xanthate process for the removal of heavy metals from wastewaters. *Water Res.*, 21: 1109.

18. Kumar, A.; Rao, N.N.; Kaul, S.N. (2000) Alkali treated straw and insoluble straw xanthate as low cost adsorbent for heavy metal removal-preparation, characterization and application. *Biores. Technol.*, 71: 133.
19. Sankararamakrishnan, N.; Dixit, A.; Iyengar, L.; Sanghi, R. (2006) Removal of hexavalent chromium using a novel cross linked xanthated chitosan. *Biores. Technol.*, 97: 2377.
20. Chauhan, D.; Sankararamkrishnan, N. (2008) Highly enhanced adsorption for decontamination of lead ions from battery wastewaters using chitosan functionalized with xanthate. *Biores. Technol.*, 99: 9021.
21. Chang, Q.; Hoa, X.; Duan, L. (2008) Synthesis of crosslinked starch-graft- polyacrylamide-co-sodium xanthate and its performances in wastewater treatment. *J. Hazard. Mater.*, 159: 548.
22. Gaballah, I.; Goy, D.; Allain, E.; Kilbertus, G.; Thauront, J. (1997) Recovery of copper through decontamination of synthetic solutions using modified barks. *Met. Metall. Trans.*, 28: 13.
23. Homagai, P.L.; Ghimire, K.N.; Inoue, K. (2010) Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse. *Bioresour. Technol.*, 10: 2067.
24. Morrison, R.T.; Byod, R.N. (1994) *Organic Chemistry*, 6th Ed.; Prentice–Hall: New Delhi, India.
25. Iqbal, M.; Saeed, A.; Zafar S.I. (2009) FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{+2} removal by mango peel waste. *J. Hazard. Mater.*, 164 (1): 161.
26. Silverstein, R.M.; Bassler, G.C.; Morril, T.C. (1981) *Spectrometric Identification of Organic Compounds*; John Wiley & Sons: New York, 95.
27. Chong, K.H.; Volesky, B. (1996) Metal biosorption equilibria in a ternary system. *Biotechnol. Bioengineering*, 49: 629.
28. Lau, P.S.; Lee, H.Y.; Tsang, C.C.K.; Tam, N.F.Y.; Wong, Y.S. (1999) Effect of metal interference, pH and temperature on Cu and Ni biosorption by Chlorella vulgaris and Chlorella miniata. *Environ. Technol.*, 20 (9): 953.
29. Krishnan, K.A.; Anirudhan, T.S. (2008) Kinetic and equilibrium modelling of cobalt (II) adsorption onto bagasse pith based sulphuric activated carbon. *Chem. Eng. J.*, 137: 257.
30. Ho, Y.S.; McKay, G. (1999) Pseudo-second order model for sorption process. *Process Biochem.*, 34: 451.
31. Li, W.; Zhang, L.; Peng, J.; Li, N.; Zhang, S.; Guo, S. (2008) Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetics studies. *Ind. Crops and Prod.*, 28: 294.
32. Winter, M.J. (1994) In: *d-Block Chemistry*, Oxford University Press, New York.
33. Hulanicki, A. (1967) Complexation reaction of dithiocarbamates. *Talanta*, 14: 1371.
34. Karnitz, Jr. O.; Gurgel, L.V.A.; De Melo, J.C.P.; Borato, V.R.; Melo, T.M.S.; De Freitas Gil, R.P.; Gil, L.F. (2007) Adsorption of heavy metal ion from aqueous single metal solution by chemically modified sugarcane bagasse. *Bioresour. Technol.*, 98: 1291.
35. Fourest, E.; Volesky, B. (1997) Alginate properties and heavy metal biosorption by marine algae. *Appl. Biochem. Bio-technol.*, 67 (1): 33.