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

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S. R. Shukla[a]; V. G. Gaikar[b]; Roshan S. Pai[a]; Umesh S. Suryavanshi[a]
[a] Department of Fibers and Textile Processing Technology, University of Mumbai, Matunga, Mumbai, India [b] Department of Chemical Engineering, Institute of Chemical Technology (Autonomous), University of Mumbai, Matunga, Mumbai, India

To cite this Article Shukla, S. R. , Gaikar, V. G. , Pai, Roshan S. and Suryavanshi, Umesh S.(2009) 'Batch and Column Adsorption of Cu(II) on Unmodified and Oxidized Coir', Separation Science and Technology, 44: 1, 40 — 62
To link to this Article: DOI: 10.1080/01496390802281984
URL: http://dx.doi.org/10.1080/01496390802281984

Separation Science and Technology, 44: 40–62, 2009
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ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802281984

Batch and Column Adsorption of Cu(II) on Unmodified and Oxidized Coir

S. R. Shukla,[1] V. G. Gaikar,[2] Roshan S. Pai,[1] and Umesh S. Suryavanshi[1]
[1]Department of Fibers and Textile Processing Technology,
University of Mumbai, Matunga, Mumbai, India
[2]Department of Chemical Engineering, Institute of Chemical Technology
(Autonomous), University of Mumbai, Matunga, Mumbai, India

Abstract: The potential of coir, a low cost lignocellulosic material, was assessed for the removal of Cu(II) ion from aqueous solutions of copper sulphate. The coir fiber was also modified by an oxidative treatment, whereby the maximum uptake of Cu(II) increased to 6.99 mg/g as compared to 2.54 mg/g for the unmodified coir. A Langmuir type of adsorption was followed by oxidized coir fiber. A second order rate equation was observed for the Cu(II) uptake. The lowering of pH adversely affects adsorption on both the materials. Almost complete desorption of the loaded Cu(II) was possible using 0.25 N hydrochloric acid. The materials retained the adsorptive capacity up to three cycles when an intermediate regeneration step was given with dilute sodium hydroxide solution. In a fixed column packed with oxidized coir fibers, it was observed that the breakthrough time decreased with an increase in inlet Cu(II) concentration. The desorption level in the fixed bed column was around 90% and the column was regenerated and used up to eight cycles. The fixed bed column packed with oxidized coir was used to remove Cu(II) from an electrochemical industrial effluent. An ion exchange mechanism has been proposed for uptake of Cu(II) on the oxidized coir fiber.

Keywords: Adsorption, coir, fixed bed, ion exchange, Langmuir, metal ion

Received 15 November 2007; accepted 15 March 2008.

Address correspondence to S. R. Shukla, Department of Fibers and Textile Processing Technology, University of Mumbai, Matunga, Mumbai, 400 019, India. Tel.: +91 22 24145616; Fax: +91 22 24145614. E-mail: sanjeevrshukla@rediffmail.com

INTRODUCTION

The use of copper stretches far back in time, which has marked the transition from the Stone Age to a more modern way of life. Even today, it is one of the most widely used heavy metals in various industries. It is used in the manufacture of copper phthalocyanine pigment with a peculiar turquoise blue color used in textile printing, as a fungicide, in the electrochemical industry, etc. Excess metal gets introduced into aquatic eco-systems as by-products of various industrial processes. The discharge of the industrial effluents into sewers without monitoring the permissible levels of the heavy metals can cause hazardous effects on living beings (1). The toxicity of metal pollution is slow and ever lasting as these metal ions are absolutely nonbiodegradable (2). Hence, the effective and economic removal of such heavy metal ions from sewage and industrial waste is inevitable.

Different methods have been proposed and are being used for the removal of heavy metal ions from industrial effluents which include chemical precipitation (3), adsorption-flotation (4), electro dialysis (5), ultra filtration (6), membrane separation (7), removal by adsorption on minerals (8,9), calcined phosphate (10), and adsorption using activated carbon (11,12). These methods are comparatively expensive and/or possess certain limitations such as a large amount of sludge formation and hence there is a need to develop cost-effective alternatives.

The assimilation of heavy metals in the agricultural products, which are cultivated, using water contaminated with heavy metals, has led to the utilization of agricultural products that have no food value, for removal of heavy metal ions through adsorption. Many attempts have been reported on heavy metal removal by bio-sorption (13,14) and adsorption on materials like agricultural by-products/biological wastes (15–17).

Our recent work on use of groundnut shells, sawdust, jute, and coir as adsorbents in their dye loaded and oxidized form has shown enhanced metal ion adsorption along with the possibility of near complete recovery of the adsorbed metal ions by desorption (18–20). The oxidative treatment, given to alginic acid also has been shown to greatly increase its adsorptive capacity for different heavy metal ions (21). The use of lignocellulosic fiber as an adsorbent for heavy metal ions is promising. Sulfuric acid treated coconut coir has been used for the adsorption of heavy metals, Pb(II), Cu(II), and Ni(II) (22). It has been reported recently that the use of a base treated juniper, a lignocellulosic fiber, has shown good removal of Cd(II) from aqueous solution (23). It has also been reported that the presence of carboxylic acid groups in eelgrass (*Zostera noltii*) has the capacity to bind copper ions from aqueous solution (24). Most of the studies using these unconventional biopolymeric adsorbents are confined to batchwise adsorption, with only a few exceptions under dynamic flow-through conditions using fixed bed columns (25–27). The present work has the advantage of using such a polymer in its original fibrous form without any further mechanical processing to increase the surface area.

The present communication reports the results on adsorption of Cu(II) on coir, a lignocellulosic fiber. The effect of oxidation of coir fibers with hydrogen peroxide on the adsorptive capacity was noted. The effect of pH on regenerative and reusable capacity of the adsorbents has been studied. The efficiency of oxidized coir for removal and recovery of Cu(II) in a fixed bed column is also assessed.

EXPERIMENTAL

Material

Coir fiber waste, collected from a local industry from Kerala, India, was washed thoroughly with cold water, dried, and cut into an approximately uniform length of 1 cm.

Chemicals

$CuSO_4 \cdot 5H_2O$ was the heavy metal salt used. The other chemicals used such as, hydrogen peroxide (50%), propanol-2, and sodium hydroxide were of analytical reagent grade supplied by Merck (India) Ltd. A standard solution of 1000 mg/l of Cu(II) was obtained from Merck (India) Ltd. Demineralized water was used for all the experiments.

Methods

Modification of Coir Fibers

Controlled bleaching of cellulosic materials with hydrogen peroxide is a common practice to destroy the naturally occurring coloring matter. Under severe conditions, oxidative degradation takes place. This oxidation converts the cellulosic hydroxyl groups present in coir to the carboxyl groups, thus creating a weak cationic ion-exchanger. The method that followed confirmed to the textile bleaching operations (28), except that the concentration of hydrogen peroxide used was higher. Thus, 100 g of the coir fiber was added to a 2 l solution containing 15 g (50%) hydrogen peroxide and 1 g NaOH (pH 11.5) at room temperature. The temperature was slowly raised to 85°C and oxidation was continued for 2 h. The material was filtered, washed thoroughly with hot water, and then with cold water. The material was then air dried and used as an adsorbent.

Estimation of Accessibility of Coir Fiber

The method used for determining the accessibility of the cellulosic materials is based on the displacement of water by propanol-2 solvent that is retained without any swelling of the material and allows the removal of extraneous liquid by centrifuging (29). The procedure is explained elsewhere (20).

IR Spectra

The IR spectra of the unmodified and oxidized coir samples were recorded with Bomem Hartmann and Braun MB Series FTIR Spectrophotometer. Samples of 100 mg potassium bromide containing 2% of finely ground powder of each sample were prepared and subjected to analysis.

Estimation of Acidic Groups in Oxidized Coir Fiber

The presence of acidic groups in the oxidized coir was estimated using methylene blue absorption method, which is commonly applied to cellulosic materials in the field of textiles (30). The same method is a reliable and established technique used for estimation of carboxylic acid groups in natural agricultural materials (24,31). The principle used is that the cellulosic material does not contain any carboxylic groups originally. On oxidative degradation of cellulose, as during oxidative bleaching, the carboxylic groups are generated. Such material is treated with a standard solution of methylene blue, a cationic dye. Colored dye cation is absorbed and retained by carboxylate anion in the oxidized cellulose.

One gram of oxidized coir was made cation-free by treating it with 1 N HCl for 10 min at room temperature followed by washing and then treating with a solution containing 100 ml of 5 mmol/l methylene blue, 15.625 mmol/l potassium dihydrogen phosphate and 10 mmol/l NaOH for 18 h. The material was filtered and the filtrate was subjected to determination of color value at λ_{max} of 664.5 nm using Techcomp UV-Vis Spectrophotometer (Model 8500, Hong Kong). A blank experiment without any material was also run alongside and the absorbance of this solution was determined. The drop in the concentration of the dye in the treated solution due to dye uptake by coir sample was determined from the calibration curve and the amount of carboxyl groups present in the coir was calculated in terms of milliequivalents/g of dry material.

Scanning Electron Micrograph

In order to study the morphological changes during bleaching of coir, the samples before and after bleaching were observed under a Scanning Electron Microscope, (Model-Philips XL 30, The Netherlands). The fibers were mounted on a specimen stub with double sided adhesive carbon tapes. The samples are very sensitive to the electron beam and the charging of the specimen causes artifacts and also focusing problem in the SEM. To avoid the charging, the specimen was coated with a thin layer (250–300Å) of conducting material viz., Au/Pd using Sputter Coater and examined under SEM at 12 KV with an angle of 45°.

Kinetic Study

The kinetics of adsorption of Cu(II) on coir fibers and oxidized coir fibers was carried out using a batch technique. The effect of agitation time was studied by shaking 1 g coir samples with 50 ml of approximately 64 and 191 mg/l solutions of Cu(II) at a pH of 5.1 and at a constant temperature of 35°C. Adsorption was continued up to 120 min with 1 ml of solution being removed at fixed time intervals for analysis of the unadsorbed metal ion. Ten sets, each of different concentrations of Cu(II) were used to avoid any inaccuracies due to the small volume change caused by removing the solution. After agitation, the adsorbent was removed by filtration and the residual solution was subjected to estimation of the unadsorbed Cu(II) using flame type Atomic Absorption Spectrophotometer, (Model 932 Plus, GBC, Australia). The amount of copper fixed by the fibers was evaluated by difference between the initial and final concentrations of Cu(II) in solution.

Adsorption-Desorption Studies

Metal ion adsorption isotherms were developed for unmodified and oxidized coir fibers from solutions that were in the concentration range from 76 to 467 mg/l of Cu(II), at a pH of 5.1. One gram of the material was shaken in a flask containing 50 ml of metal ion solution at a constant temperature of 35°C using a flask shaker for a predetermined equilibrium time of 120 min. The material was then filtered and the residual solution was analyzed for Cu(II) concentration using an Atomic Absorption Spectrophotometer. In the case of the oxidized coir, the residual solution was analyzed for Na(I) also. The standards for analysis were prepared from stock solutions of 1000 mg/l supplied by Merck (India) Ltd.

All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no adsorption was taking place on the walls of the apparatus used.

Experiments were also conducted at different pH by adjusting the initial pH to the lower ones by using 0.25 N HCl. Thus, initial pH of 5.1 of Cu(II) solution was adjusted to 3.5, 2.6, and 1.1.

Desorption of the Cu(II) from each of the loaded material was carried out by shaking them with 50 ml of 0.25 N HCl at 35°C for 120 min. The metal ion contents of the desorbed acid solutions were estimated using the Atomic Absorption Spectrophotometer.

Regeneration of Coir Samples

The unmodified and oxidized coir samples after desorption of metal ions were thoroughly washed with demineralized water and were treated with 50 ml of 32 mg/l NaOH solution for 60 min. This step was followed by washing again with demineralized water, drying, and reusing the material for adsorption. The experiment was also carried out without treatment with NaOH.

Fixed Bed Column Study

Adsorption Cycle. The oxidized coir, which had a higher uptake of Cu(II) ion was used for adsorption in a fixed bed column. One hundred gram of oxidized coir was filled in a glass column of 4.8 cm inner diameter to yield a bed length of 43 cm. Glass beads were used as support at the bottom and top. The solution containing known concentration of Cu(II) ion was fed from the bottom using a peristaltic pump (Electrolab, Mumbai). A constant flow rate of 40 ml/min was used for the entire study. The liquor coming out from the top was collected at regular intervals and the amount of Cu(II) adsorbed was estimated. Three different Cu(II) concentrations of 73, 153, and 470 mg/l were used in the present study. Breakthrough curves were developed by plotting C/C_o vs t, where C_o and C are the inlet and outlet concentrations of Cu(II) in mg/l and t is time in min.

Desorption Cycle. After adsorption, the column was washed with demineralized water to remove any unabsorbed Cu(II). This was followed by desorption using 0.25 N HCl. The amount of the acid was calculated stoichiometrically and a slight excess (5%) was added in order to ensure complete desorption of Cu(II). The feed was given from the top of the column and the flow rate of acid addition was kept constant at 10 ml/min. The acid addition was followed by addition of demineralized water, which serves the purpose of removing the desorbed Cu(II) ion and clearing off the acidity of the bed. The addition of water was continued till the Cu(II) concentration coming out was less than 1.90 mg/l. The liquor coming out at the bottom of the column was collected at regular intervals (t) and was analyzed to quantify Cu(II) desorption (C). Desorption curves were developed by plotting C vs t.

The concentration factor was calculated as the ratio of desorbed Cu(II) concentration to initial Cu(II) concentration in mg/l.

Regeneration and Reusability Study of Fixed Bed Column. The regenerative treatment was given to the adsorbent after complete desorption of Cu(II) was achieved. One liter of 0.025 N NaOH was circulated in the bed with a flow rate of 40 ml/min. The final step was washing the column with 600 ml of demineralised water.

The adsorption, desorption, and the regeneration step was considered as one cycle. The reusability of the column was studied for 8 such cycles with an initial Cu(II) concentration of approximately 153 mg/l.

Adsorption of Cu(II) from Electrochemical Industry Effluent. The adsorption, desorption, and the regeneration study was also carried out for an electrochemical industry effluent having 141.3 mg/lof Cu(II) and 2.23 Mg/l of total Fe. The effluent was highly acidic (pH 1.5) and hence it was partially neutralized using NaOH (1.2 mg/l). At a pH of nearly 4, the solution became turbid, which is due to the precipitation of ferric hydroxide. The pH was kept at 5.1 so as to avoid precipitation of Cu. The solution thus obtained was filtered to remove the precipitate of ferric hydroxide and used for adsorption in a fixed bed column filled with oxidized coir.

RESULTS AND DISCUSSION

Characteristics of the Coir Fibers

Coir, a lignocellulosic fiber, possesses a substantial amount of cellulose (43.44%) and lignin (45.84%) (32). In our previous work, coir fiber has been successfully used for adsorption of Pb(II) from aqueous solutions (19). The uptake of metal ions by lignocellulosic materials was observed to be electrostatic in nature and even dilute acids are capable of fully desorbing them (33). In the present study, the coir was subjected to a chemical modification by oxidation using hydrogen peroxide. Both unmodified and modified coir, cut uniformly, were used as adsorbents.

The propanol-2 retention values for unmodified and oxidized coir are 19.12 and 44.56%, respectively. This technique of accessing the openness of the cellulosic materials has long since been used for estimating their swelling caused by various intercrystalline swelling agents (29). The key factor is that on treating cellulosic material with a swelling agent, the fiber structure swells laterally due to breaking of inter-chain hydrogen bonds in the amorphous region of the polymer, thereby moving the polymer chains apart. This makes it possible for Propanol-2 to simply imbibe in by displacing the swelling agent without altering the swollen structure. The technique gives precise understanding about the changes in the accessibility of the cellulose containing material, more or less in a comparative manner, caused by any modification. In the present case, it is expected that apart from the chemical nature of the adsorbing material, the openness or accessibility of its physical structure also has an important role to play in allowing the metal ions to be adsorbed on the external surface as well as internal crystallite surfaces of the polymer by penetration. The higher Propanol-2 retention value of the oxidized coir material indicates that it has more accessibility than the unmodified one.

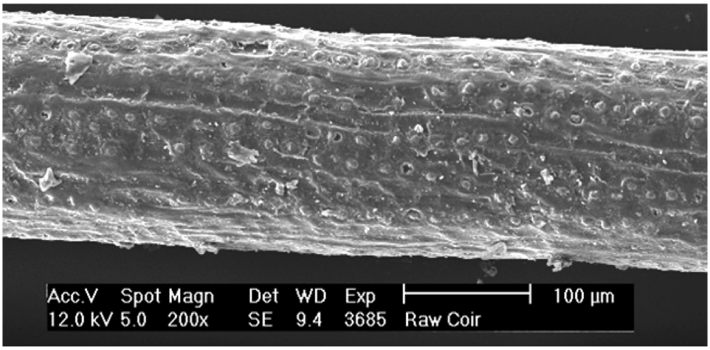
The same phenomenon can also be observed from the SEM of unmodified and oxidized coir samples shown in Fig. 1. The oxidized coir clearly shows more number of pores, which have opened up due to oxidation when compared to the unmodified coir.

Oxidation of the cellulosic part in coir causes its degradation leading to chain scission and generation of carboxyl groups. The lignin component upon oxidation gives rise to water-soluble dicarboxylic acids. Overall, the oxidation of coir led to some loss in the strength, although not high enough to distort its physical (fibrous) form. The carboxylic acid groups of the oxidized coir are capable of quantitative absorption of methylene blue. The carboxylic acid content estimated using methylene blue absorption studies indicated a higher amount of carboxylic acid groups (0.2121 meq/g) in oxidized coir fibers when compared to unmodified coir (0.0704 meq/g).

Figure 2 gives the IR plot of unmodified coir fibers. The IR plot in Fig. 3, for the oxidized coir, shows a peak at $1735.34\,\mathrm{cm}^{-1}$, which is characteristic of the carbonyl group of –COOH, formed due to the oxidative treatment of coir.

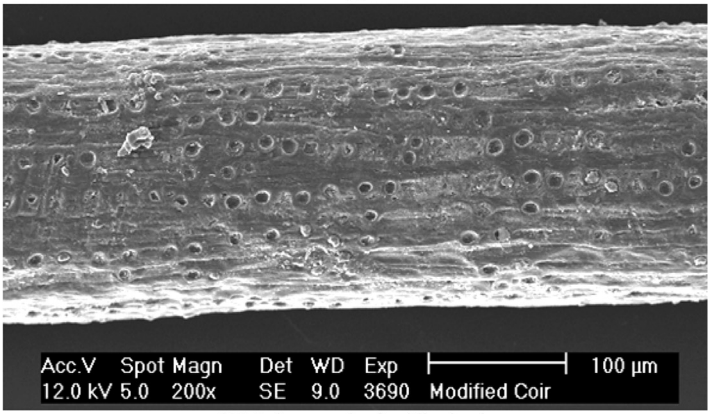
Adsorption Kinetics

Figure 4 shows the effect of time on batch adsorption of Cu(II) up to 120 min for the unmodified and oxidized coir fibers from



SEM photograph of coir fibre

(a)



SEM photograph of oxidised coir

(b)

Figure 1. SEM of coir samples.

aqueous solutions of 76 and 207 mg/l Cu(II). It may be observed that irrespective of the concentrations and the materials used during the study, the adsorption reached an apparent equilibrium after about 90 min. The time profile of Cu(II) uptake is a continuous curve leading to saturation, suggesting the possible monolayer coverage on the surface.

The application of second order reaction kinetics, equation (1), to the overall rate of the sorption process can be used to assess the dependency of the process on the sorbed Cu(II) concentration. The Lagergran rate equation is the most widely used sorption rate equation for the sorption of solutes from a liquid solution (14). If the rate of sorption is

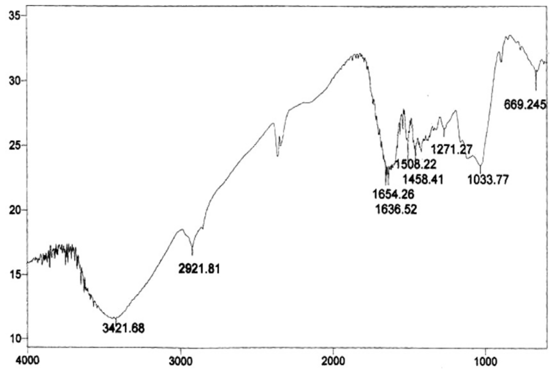


Figure 2. IR spectra of coir fibers.

a second order mechanism, the pseudo-second order kinetic rate equation for chemisorption may be expressed as

$$\frac{dQ_t}{dt} = k_2(Q_e - Q_t)^2 \tag{1}$$

Where, k_2 is the over all rate constant for the adsorption process (g/mg/min), Q_e is the amount of Cu(II) adsorbed at equilibrium (mg/l), and Q_t is the amount of Cu(II) adsorbed at time t (mg/g). Integration of this equation leads to equation (2)

$$\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_e}t \tag{2}$$

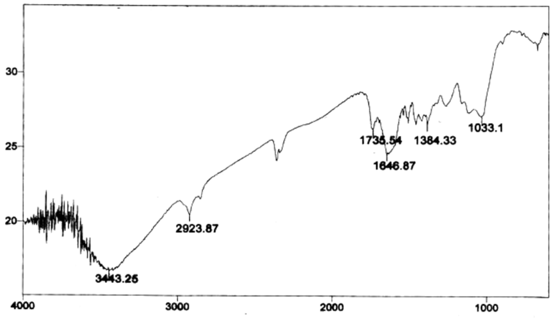


Figure 3. IR spectra of oxidized coir fibers.

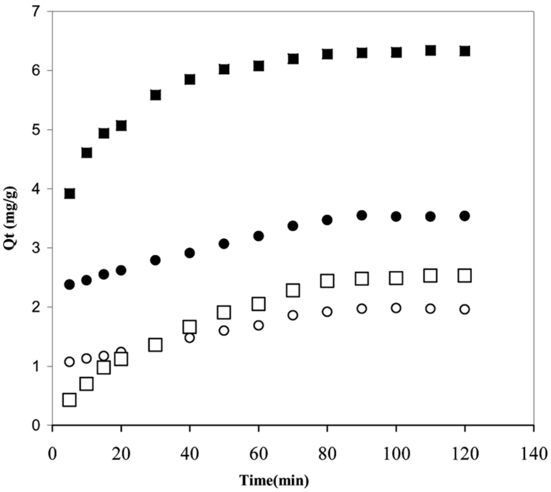


Figure 4. Effect of time and initial concentration on adsorption of Cu(II) on coir samples; ○ Cu(II) uptake on coir fibers from 76 mg/l Cu(II) solution; ● Cu(II) uptake on oxidized coir fibers from 76 mg/l Cu(II) solution; □ Cu(II) uptake on coir fibers from 207 mg/l Cu(II) solution; ■ Cu(II) uptake on oxidized coir fibers from 207 mg/l Cu(II) solution.

Where, h is the initial sorption rate [mg/g/min] and is given by

$$h = k_2 Q_e^2 \tag{3}$$

The rate parameter k_2 and Q_e can be directly obtained from the intercept and slope of the plot of t/Q_t against t. The second order plots (Fig. 4) gave good compliance with a second order rate equation for Cu(II) adsorption on unmodified and modified coir samples. These results are similar to our previous studies for removal of Pb(II) using different coir fibers (19). The application of the second order fit has also been reported for the removal of Cr(III) by biosorption on cork powder (34), Pb(II) removal using sugar beet pulp (35) and Pb(II), Cu(II), and Ni(II) on Sphagnum moss peat (36). These results suggest that the pseudo-second order adsorption is predominant.

Table 1 indicates that the initial sorption rate, h, decreased in the case of unmodified coir whereas it showed an increase in the case of oxidized coir, at higher Cu(II) concentration. The values of the overall sorption rate constants, $k_{2,}$ were found to decrease in both the cases when the initial concentration of Cu(II) was increased from 76 to 207 mg/l.

Table 1. Pseudo-second order parameters for Cu(II) adsorption on different coir fibers

Material	C_0 (mg/l)	k_2 (g/mg/min)	h (mg/g/min)	r^2
Coir	76	0.0369	0.1708	0.9781
	207	0.0065	0.0843	0.9827
Oxidized	76	0.0377	0.5167	0.9915
coir	207	0.0303	1.3691	0.9997

Adsorption Isotherms

The equilibrium uptake of Cu(II) ions by coir samples increased with time and initial concentration of the Cu(II) ions in solution as shown in Fig. 4. Figure 5 shows the adsorption isotherm with a dotted line indicating Langmuir model. The experimental data were applied to a Langmuir isotherm, described by equation

$$Q_e = \frac{Q_o b C_e}{1 + bC_e} \tag{4}$$

Where, C_e is the equilibrium concentration (mg/l), Q_e is the amount adsorbed (mg/l) at equilibrium, and Q_0 and b are the Langmuir constants related to the adsorption capacity and the energy of adsorption,

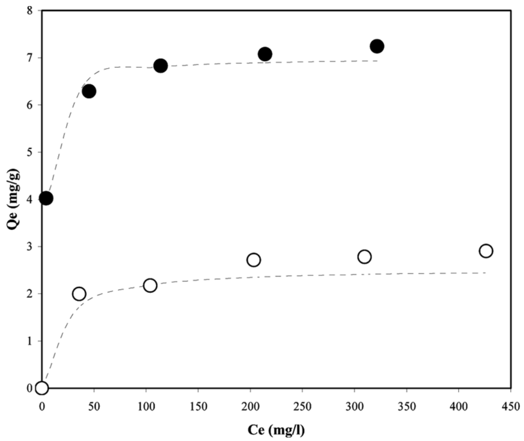


Figure 5. Adsorption isotherm for Cu(II) on coir samples; ○ Cu(II) adsorption on coir fibers; ● Cu(II) adsorption on oxidized coir; ------ Langmuir model.

respectively. The plots of C_e/q_e vs C_e, for coir samples obtained were found to be linear (Figure not shown). The maximum adsorption capacity Q_0 and the energy of adsorption b were calculated from the slope and the intercept of these straight-line plots, which were 2.54 mg/g and 0.059 l/mg, respectively, for unmodified coir, whereas for the oxidized coir, the respective values were 6.99 mg/g and 0.308 l/mg. A comparison of the maximum adsorption capacities of various natural adsorbents with our results is given as Table 2.

The experimental data were submitted to the Freundlich model, which is expressed as

$$\log_{10} Q_e = \log_{10} K_f + \frac{1}{n}\log_{10}\,(C_e) \qquad (5)$$

Where, C_e is the equilibrium concentration (mg/l) and Q_e is the amount adsorbed (mg/g) at equilibrium time. K_f and n are the Freundlich constants, n giving an indication of favorability and K_f [$mg^{(1-1/n)}$ $lit^{1/n}/g$], the capacity of the adsorbent.

The K_f and n values for unmodified coir were 0.0336 and 6.09, respectively, whereas the corresponding values for oxidized coir were 0.0957 and 7.23.

It may be observed that the determination coefficient, r^2 value calculated for the Freundlich isotherm for unmodified coir was 0.9366 where as that for the oxidized coir, it was 0.9486. The Langmuir isotherm exhibited an extremely high correlation value of 0.9906 only in the case of the oxidized coir fiber. A lower r^2 value of 0.8147 was observed in the case of unmodified coir fiber. The main characteristic of the Langmuir isotherm is that it is based on the assumption that all the sites have equal adsorption energies. The lines in Fig. 5 represent the modeled results using Langmuir equation. The conformity of the adsorption data of Cu(II) uptake by the oxidized coir with the Langmuir model indicates the better homogeneity of the binding sites after the oxidation treatment.

Table 2. Comparison of Cu(II) adsorption capacities on various reported adsorbent

Adsorbent	Cu(II) uptake (mg/g)	References
Coca Shell	2.90	37
Papaya wood	19.90	38
Chaff	1.98	39
Peat Biomass	25.42	40
Sugar beet pulp	20.95	41
Saw dust	4.90	42
Oxidized coir	6.99	Present work
Banana Peel	4.80	43

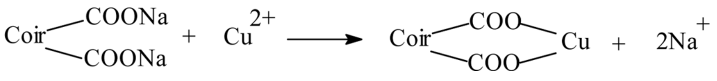
The higher b values for the oxidized coir than the unmodified coir indicate higher affinity of the former towards Cu(II) ions. This indicates that the Cu(II) ion affinity towards the adsorbing material was enhanced significantly after the oxidative modification.

Mechanism of Cu(II) Uptake

The coir fiber contains a cellulose component, which is a natural polymer made up of β-glucose units with abundant primary and secondary hydroxyl groups and lignin having a network type of structure with majority of polyphenolic, methoxy, and free hydroxyl groups that are known to adsorb metal ions (44).

The increase in the adsorption of metal ions in the case of the oxidized coir has been attributed to the formation of carboxylic acid groups due to oxidation treatment. The oxidation process using hydrogen peroxide was carried out in an alkaline medium (pH 11.5) and hence these carboxyl groups also will be in the form of their sodium salt. It was observed that during the uptake of Cu(II), there was release of Na(I) from the oxidized fiber. The release of Na(I) was maximum (4.20 mg/g) at the highest initial concentration of Cu(II) used in the present study and the amount of Cu(II) fixed on the oxidized fiber at this concentration was 7.18 mg/g. Thus one Cu(II) ion replaces two Na (I) cations.

The same has been shown in Fig. 5. The metal ion adsorption on oxidized coir, based on ion exchange mechanism can be expressed as



$$\text{Coir}\begin{cases}\text{COONa}\\ \text{COONa}\end{cases} + \text{Cu}^{2+} \longrightarrow \text{Coir}\begin{cases}\text{COO}\\ \text{COO}\end{cases}\text{Cu} + 2\text{Na}^{+}$$

The other reason for the enhancement in the uptake of Cu(II) in the case of oxidized coir may be attributed to the increase in pore size which is clear from the SEM photograph (Fig. 1) and high accessibility which is evident from the high Propanol-2 retention value.

Effect of pH on Cu(II) Uptake

The coir samples showed a low affinity for Cu(II) adsorption under acidic conditions, and the adsorption decreased with lowering of the pH. Thus, Cu(II) ions having a maximum adsorption of 29.44% at pH 5.1 showed a progressive decrease to 16.85% at a pH of 3.5, 5.36% at pH of 2.6, and finally 1.02% at a pH of 1.1 for the unmodified coir.

The corresponding values for oxidized coir were 75.71%, 55.61%, 32.31%, and 6.32%, respectively. The low uptake of Cu(II) at a lower pH may be due to the competition between the H^+ and the metal ion. This behavior was utilized to desorb Cu(II) and to regenerate the sorbents for subsequent applications.

Desorption and Regeneration Study

Table 5 shows the adsorption and desorption efficiencies of coir samples from a solution of 147 mg/l Cu(II). Desorption was nearly complete for the unmodified as well as for the oxidized coir.

The coir samples were then subjected to adsorption-desorption cycles through a regeneration step in between. It can be clearly observed from the data in Table 3 that the efficiency of adsorption was retained only when the materials after desorption were given a treatment with 0.025 N NaOH solution. When the desorbed materials were reused without such intermediate treatment, there was in fact a decrease in the adsorptive capacity of the materials.

Thus, Cu(II) ions showed 29.44% adsorption on unmodified coir, which decreased to 9.09% when it was subjected only to washing with water after desorption. However, when the desorbed coir was subjected to regeneration using NaOH, the readsorption values were 28.62, 29.19, and 29.35% after each of the three adsorption-desorption-regeneration cycles indicating nearly the same adsorption as that of the original material. Oxidized coir fibers followed the same trend.

There occurs a lowering of pH during adsorption of metal ions on to cellulosic materials due to the release of H^+ ions from cellulose into the solution. Desorption occurs by the replacement of metal ions by H^+ ions from the eluting acid. It can be seen that there was a substantial lowering of pH after adsorption, as indicated in Table 3. When the coir samples were subjected to re-adsorption, the drop in pH was still higher. This may be due to the replacement of H^+ ions from the materials by the metal ions. The difference in pH before and after adsorption was found to be minimal in the case of oxidized coir adsorbent when it was used in the first adsorption cycle. The oxidation of coir fibers has been carried out in an alkaline medium resulting in the formation of sodium salt of carboxylic acid groups. In the case of desorbed materials regenerated with NaOH solution, Na^+ is released into the solution during readsorption, which has no role in changing the pH to acidic. Hence in this case the pH change during adsorption was not prominent. Therefore, a loading with Na^+ appears to be essential after desorption and washing, i.e., the alkali regeneration step to retain the original adsorption capacity of the material.

Table 3. Adsorption and desorption of Cu(II) ion from solution with initial 147 mg/l Cu(II) concentration

			Regeneration step							
			Metal ion adsorbed (%)							
				With NaOH					pH of final bath after adding desorbed material	
Adsorbent	Ads. (%)	Desorbed (%)	Without NaOH	Cycle 1	Cycle 2	Cycle 3	Initial bath	Final bath	Without regeneration	With regeneration
Coir	29.44	96.29	9.09	28.62	29.19	29.35	5.1	4.41	3.02	4.45
Oxidized coir	75.71	98.29	22.11	75.81	75.72	75.90		5.03	3.13	5.08

Uptake of Cu(II) in a Fixed Bed Column

Removal of Cu(II) from aqueous solution was also studied in a fixed bed column. In the batchwise method the oxidized coir gave a higher uptake of Cu(II) when compared to the unmodified coir. Hence, only the oxidized coir was used in the fixed bed column study. The effect of three different initial Cu(II) concentrations of 73, 153, and 471 mg/l were studied using a fixed bed column at a flow rate of 40 ml/min. The column loading capacity was determined from the breakthrough curves. Experiments for Cu(II) removal in fixed bed column were also performed using an actual sample of electrochemical wastewater containing 141.3 mg/l Cu(II).

It can be seen from the breakthrough curves (Fig. 6) that as the initial concentration of the Cu(II) is increased, the break through time decreased. Thus, with a lower concentration of 73 mg/l of Cu(II) it was possible to operate the column for approximately 100 min till the breakthrough point, whereas when the highest Cu(II) concentration of 471 mg/l was used, the break through time decreased to 25 min. Maximum loading of the bed was, however, obtained when the highest Cu(II) concentration was used. The column was more saturated at the lower inlet concentration of Cu(II) which can be seen from the values of the degree of saturation of the bed given in Table 4.

The results for Cu(II) removal from the actual effluent using a column packed with an oxidized coir sample are also plotted in Fig. 6. Table 4 indicates that the total Cu(II) uptake from the effluent was 583.2 mg/100 g of oxidized coir, which is comparable with the Cu(II) uptake when synthetic effluent of inlet Cu(II) concentration, 153 mg/l was used.

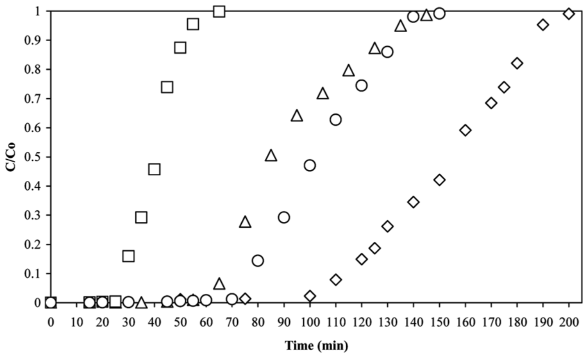


Figure 6. Breakthrough curves for adsorption of Cu(II) in a fixed bed column packed with oxidized coir; ◇ Cu(II) concentration 73 mg/l; △ Cu(II) concentration 153 mg/l; □ Cu(II) concentration 471 mg/l; ○ Cu(II) concentration 141 mg/l (Effluent).

Table 4. Uptake and desorption of Cu(II) in a fixed bed column

Initial conc. (mg/l)	Cu(II) adsorbed up to breakthrough point (mg/100 g)	Total Cu(II) adsorbed (mg/100 g)	Degree of saturation (%)	Amount of HCl used for desorption (ml)	Amount of water added (ml)	Cu(II) desorbed conc. (mg)	Desorption (%)	Total concentration factor
73	316.6	438.3	72.23	75	725	432.8	98.74	7.38
153	361.3	552.6	65.38	75	725	501.0	90.57	4.09
447	471.0	752.7	62.57	100	900	675.5	89.74	1.43
141.3*	407.0	583.2	69.78	75	725	505.6	86.69	4.47

*Cu(II) from Effluent.

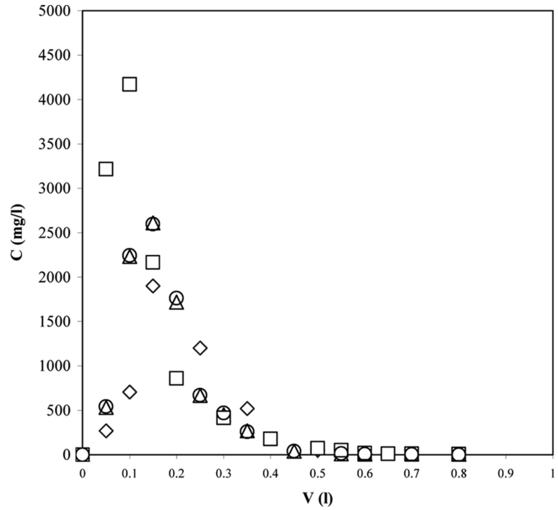


Figure 7. Desorption curves of Cu(II) from a fixed bed column packed with oxidized coir; ◇ Desorbed from bed adsorbed with 73 mg/l of Cu(II); △ Desorbed from bed adsorbed with 153 mg/l of Cu(II); □ Desorbed from bed adsorbed with 471 mg/l of Cu(II); ○ Desorbed from bed adsorbed with 141 mg/l of Cu(II) (Effluent).

Desorption of Cu(II) from the Fixed Bed Column

The desorption curves for Cu(II) from the bed after adsorption cycle, using 0.25 N HCl, are plotted in Fig. 7. The exact amounts of acid and demineralized water used for elution can be obtained from Table 4. The desorption level was quite high in almost all the cases and it was almost complete when desorbed from the bed loaded with Cu(II) from the lowest

Table 5. Regeneration and repeated use of fixed bed column for Cu(II) uptake

	Cu(II) concentration			
Cycle no.	Initial (mg/l)	Adsorbed (mg)	Desorbed (mg)	Desorption (%)
1	153	553	501	90.57
2	156	548	495	90.25
43	156	540	490	90.69
44	156	542	491	90.61
45	152	535	497	92.87
46	154	547	493	90.12
47	156	539	490	90.91
8	157	537	495	92.18

initial concentration. A concentration factor of more than 7 was achieved when the lowest initial Cu(II)concentration 73 mg/l was used. It can be observed that the concentration factor was dependent on the initial concentration and it decreased with an increase in the initial concentration.

In the case of the actual effluent, it was possible to remove Cu(II) and to desorb it with a concentration factor of nearly 4.5.

Repeated Adsorption-Desorption of the Fixed Bed Column

The cost incurred in modifying the coir fibers is justified by enhanced Cu(II) uptake by the oxidized coir fibers and it is advisable to reuse the adsorbent as many times as possible which has the advantage of bringing down the cost of the process. The reusability of the column was studied for 8 cycles with an initial concentration of approximately 153 mg/l of Cu(II) at a pH of 5.1. It can be seen from Table 5 that the adsorption and desorption values were almost constant up to eight cycles.

CONCLUSION

The oxidative modification of coir fibers was much more effective in removing Cu(II) from the aqueous solution with a maximum uptake capacity of 6.99 mg/l. The adsorption obeyed a pseudo-second order kinetics and followed the Langmuir adsorption isotherm. With decreasing pH the sorption capacity decreased. The sorption capacity of both unmodified and oxidized coir fibers decreased with decreasing pH. Nearly complete desorption followed by repeated use of the coir samples was possible with an intermediate alkaline regeneration step. Removal of Cu(II) from an electroplating waste industry effluent was also achieved to the same level. A reversible ion exchange mechanism is proposed for the uptake of Cu(II) by the oxidized coir fibers.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the financial support given by Ministry of Environment and Forests, Govt. of India, New Delhi.

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