Characterization of chemically modified corncobs and its application in the removal of metal ions from aqueous solution

M. Nasiruddin Khan *, M. Farooq Wahab

Department of Chemistry, University of Karachi, Karachi 75270, Pakistan

Abstract

The objective of this work was to convert corncobs to activated carbon by low temperature chemical treatment for removing copper from wastewater. The parameters for developing a new adsorbent i.e. sorption capacity, selectivity, regenerability, suspension test, and kinetics were investigated. All studies were performed in batch experiments. Removal of copper from aqueous solutions varied with the amount of adsorbent, metal ion concentration, agitation time, solution pH and the species of copper present. It was found that the effect of temperature was very small. The Langmuir model was found to best fit the equilibrium isotherm data. Kinetics of copper removal at two different temperatures obeyed Lagergren pseudo-first-order equation. Effect of water hardness, other cations (Pb^{2+} and Zn^{2+}) on copper removal was also studied. Experiments with anionic and cationic complexes of copper showed that anionic copper species are not removed at all by the prepared material. To observe the nature of surface and pore structure scanning electron microscope (SEM) images of modified corncobs were used. To study the interaction forces between the adsorbent and the metal ion functional group analysis with infrared spectroscopy and proximate analysis were carried out. In addition, recovery of the metals ion and regeneration of spent adsorbent was possible by acidified hydrogen peroxide. Since the uptake capacity of the prepared adsorbent is 26 mg Cu/g for copper, it can be a potential adsorbent for removing and recovering other heavy metal ions from contaminated wastewaters. The sorption capacity of the treated corncobs for copper was better than the reported capacity of other activated carbons prepared from agricultural sources.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Corncob; Chemical modification; Characterization; Copper; Sorption; Multicomponent system; Regeneration

1. Introduction

Rapid industrialization throughout the world has generated huge volumes of wastes containing toxic materials, such as heavy metals, dyes, phenols and surfactants. The presence of heavy metals in wastewater and surface water is major concern of the public health and the environment. The increased use of metals and chemicals in the process industries have resulted in the generation of large quantities of aqueous effluents that contain high levels of metals, creating serious environmental disposal problems. Additionally, mining, mineral processing and extractive metallurgical operations generate huge volumes of toxic liquid waste [1]. Treatment of high volume wastewater containing low concentrations of pollutants is becoming increasingly important as the discharge regulations become more stringent [2].

Copper and its salts are widely used industrial chemicals as agricultural fungicides, petroleum refining, electroplating baths and in pigments. Mining wastes and acid mine drainage contribute significant quantities of dissolved copper to effluent streams [11]. Copper usually occurs in nature as oxides and sulfides. In acidic environments, free aqueous Cu^{2+} dominates. At pH 6–8, the predominant species are Cu^{2+}, $Cu(OH)_2$, $CuHCO_3^+$, $CuCO_3$, and $CuOH^+$, while at pH > 10 the major species are $Cu(OH)_2^{4-}$ and $Cu(OH)_3^-$ [3]. Copper is essential to human life and health but, like all heavy metals, is toxic as well [4]. Copper may be found as a contaminant in food, especially shellfish, liver, mushroom, nuts and chocolate. Excess copper in the human body can cause stomach and intestinal distress such as nausea, vomiting, diarrhea and stomach cramps.

The average concentration of copper in lakes, rivers and groundwater is about 4 μg/L. However, in few cases groundwater also contains higher levels of copper due to human activities. The Environmental Protection Agency (EPA) sets a limit of 1.3 mg Cu/L in drinking water and the allowed industrial dis-

---

* Corresponding author. Tel.: +92218265743.
E-mail address: khannasir@myway.com (M. Nasiruddin Khan).

charges level of copper should not exceed 1 mg/L, otherwise the water has a metallic taste.

A number of methods exist for the removal of heavy metals from liquid wastes when they are present in high concentrations. These include coagulation, precipitation, evaporation, ion-exchange, membrane processes and biosorption [5–7]. Among the different physicochemical processes, sorption has shown to be the best prospects for overall treatment owing to its economical feasibility and environmental friendly behavior [8–10]. Some workers have successfully used biosorbents such as Kraft lignin for heavy metal removal form aqueous system which shows quite high adsorption capacity for cadmium and copper [11]. Commercial activated carbon is widely used for the removal of heavy metals, but its high capital and regeneration cost has encouraged researchers to seek a new and cheap adsorbents.

In this study, activated carbon was prepared from corncob, a local agricultural by-product of *Zea mays* plants and abundantly available cheap feedstock. Vaughan et al. [12] have chemically analyzed the corncobs and showed that it mostly consists of cellulose, hemicellulose and a small fraction of lignin. They studied the removal of metals including copper by untreated, water-washed, sodium hydroxide treated and acid washed corncobs but did not report regeneration and removal of other copper species besides the Cu^{2+} ion. Sorption without regeneration is not viable because it merely transfers the contaminant from one phase to another. Dried and powdered corncobs tend to form thick slurry in water due to its starch content and its property of swelling in water and therefore need pretreatment. The powdered corncob in this study was carbonized with sulfuric acid, utilizing its dehydrating and oxidizing action on organic materials, and then thermally treated for improving its sorption capacity. The carbonized material was then tested for copper removal under varying conditions. The influence of pH, agitation rate, dose of adsorbent, chelating agents, and temperature was investigated and its potential use for industrial waste water treatment using a synthetic and a real industrial sample. An attempt was also made to study the influence of copper removal in the presence of competing metal ions. Recycling of the adsorbent was also carried out with hydrogen peroxide under acidic conditions.

2. Experimental

2.1. Quality assurance/control

To establish the accuracy, reliability, and reproducibility of analytical results, the reagents employed were of highest purity and the volumetric glassware employed for dilution and solution preparation was of class "A" quality. The experimental blanks were used when necessary. The batch experiments were run once. The AAS Cu standard was obtained from May & Baker Ltd., England. The Perkin-Elmer atomic absorption spectrophotometer-2380 was operated at the wavelength at maximum sensitivity (0.077 mg/L), 324.8 nm with slit width of 0.7 nm and the analysis was carried out the linear range of copper. Before the analysis, the AAS were optimized by sensitivity check (4.0 ppm) copper standard to display an

absorbance of 0.2 units on the instrument. The spectrophotometer readings were averaged thrice with an integration time 3 s to obtain better precision. Dilutions where necessary, were made in approximately 1% HNO_3 to avoid adsorption of metal on the glassware surface and prevent copper precipitation. The Perkin-Elmer quartz wool was used in filtering pipette (because filter papers were adsorbing copper significantly) to simultaneously filter and measure required volume. The pipette was washed with dilute HNO_3 prior to use and initial volume was discarded [13]. The glassware were washed as described in Ref. [14] followed by rinsing with distilled water and air-dried.

2.2. Materials

Corncob used in the preparation of the activated carbon was obtained from a local vegetable market. Sulfuric acid from Riedel-de-Häen of extra pure quality having 95–97 assay value (density 1.84 g/mL) was used for the preparation of activated carbon. The working stock 1016 Cu^{2+} mg/L solution was prepared by dissolving 1.0161 g of pure copper wire in 15 mL of pure concentrated nitric acid and diluting to mark in 1 L volumetric flask with distilled water and diluted accordingly.

2.3. Method

Corncob carbon was prepared by treating the milled corncobs with 1.8 times weight of sulfuric acid (18 M) and heated for 24 h at 150 °C. It was washed several times with distilled water over a Büchner funnel to remove remaining sulfuric acid, till the washings became neutral to litmus and dried in an oven at 100 °C for 6 h. The mesh size of the dried material was 80–100.

Batch mode sorption experiments were carried out with 0.50 g of adsorbent and 50 mL of copper(II) solution in 250 mL Erlenmeyer flasks with an agitation rate of 125 rpm. The pH of the solution was adjusted with 0.01 M nitric acid or potassium hydroxide. The flasks were placed on an orbital shaker at a constant speed of 125 rpm, and the solutions filtered using a filtering pipette. To optimize the removal of copper, experimental runs were carried out to determine the equilibrium time, agitation speed, optimum pH and adsorbent dose.

The sorption capacity q in mg Cu/g of adsorbent was calculated by mass balance equation. The equilibrium isotherm were determined at 31 ± 1 °C under optimized conditions in the concentration range of 50–1000 mg/L. Sorption kinetic studies were carried out at 31 ± 1 and 45 ± 1 °C with 100 mg/L Cu, after adjusting pH at 2.0 (low pH was adjusted intentionally to slow down the sorption process) in the time interval of 0.5–60 min.

Acidified hydrogen peroxide was a regenerating solution made by 1 mL of 33% H_2O_2 and 1 mL of 65% HNO_3 diluted to 100 mL. Regeneration of adsorbent was carried out by treating the loaded material with 10 mL regenerating solution per gram of the adsorbent was used batch-wise in four cycles with 100 mL of 250 mg/L copper solutions each time. The corncob carbon after adsorption was filtered over a Büchner funnel and transferred quantitatively to the regenerating solution

and stirred with magnetic bead for 15 min. It was then re-filtered washed with distilled water to remove hydrogen peroxide and nitric acid; oven dried at 104 °C and used again for the subsequent experiments. Percentage removal of copper was evaluated.

Moisture, ashes, volatile matter and pH (of aqueous slurry) were determined by ASTM (1995) [15]. The gross calorific value (also known as High heating value HHV) was determined by ASTM method (D 2015-96) in a bomb calorimeter. Elemental analysis (C, H, S, and N) was carried out in a Perkin-Elmer, PE-2400 analyzer. The FT-IR Spectrum was recorded on Thermo-Nicolet, IR-100 spectrophotometer in the range of wavenumbers between 4350 and 350 cm^{-1} at resolution of 4 using 16 scans. The sample disc was prepared by mixing the corncob carbon with oven dried IR grade KBr in a 1:600 (w/w) ratio. The scanning electron microscope (SEM) images of the surface corncob carbon were taken on JEOL JSM-6380, analytical scanning microscope. The corncob carbon was first gold coated (300 Å thickness) with ion sputtering device and then observed under the microscope.

The suspension test of the corncob carbon, to provide a quick and reliable way of determining the pH point of zero charge (pH$_{PZC}$), was carried out using the pH drift method used by Yang et al. [16], with the modification that sodium chloride was used as an inert electrolyte. Prior to measurement of pH drift, the corncob carbon was thoroughly washed with water followed by dilute sodium hydroxide (∼pH 10) to neutralize any free sulfuric acid that may have remained and finally soaked in HCl for 24 h. After filtration, it was washed with distilled water till the filtrate was free of chloride and sulfate ions as detected by AgNO$_3$ and barium sulfate tests. The "enriched" corncob carbon was then air-dried. This was done to ensure the removal of any potential effects on pH drift due to dissolution of salts in corncob carbon. The pH of test solutions was adjusted in 0.005 M NaCl in the range between 1.92 and 10.90 using 0.5 M HCl or 0.5 M NaOH. A 0.06 g of corncob carbon was added into 20 mL of the pH-adjusted solution in a plastic capped vial and equilibrated for 24 h. The final pH was measured and plotted against the initial pH. The pH at which the curve crosses the pH$_{initial}$ = pH$_{final}$ line was taken as pH$_{PZC}$.

3. Results and discussion

Various methods of preparing adsorbents based on activated carbon are described in Kirk–Othmer Encyclopedia of Chemical Technology [17]. However, these methods require anaerobic pyrolysis (heating at high temperature in the absence of air) of pre-treated material in the presence of argon or nitrogen atmosphere. Therefore, in this work we tried chemical activation combined by low temperature heating to make the process environmental friendly. It was observed that treatment with concentrated sulfuric acid alone was not sufficient, as checked by its ability to remove metals and dyes, though the material was completely carbonized by the acid; heating at 150 °C was needed to convert the carbonized material into porous sorbent.

Table 1
Data of chemical and physical properties of chemically treated adsorbent

Proximate analysis (wt.%)	
Moisture	17.0 ± 0.66
Volatile matter	41.53 ± 1.23
Ashes	3.21 ± 0.05
Fixed C	37.62 ± 4.32
Elemental analysis (wt.% of dried material)	
C	71.31
H	1.52
N	0.83
S	0.55
Physical parameters	
Pore dimensions (from SEM)	$31.4 \mu m \times 23.8 \mu m$
pH of aqueous slurry	3.01
Gross calorific value (HHV)	4095 ± 9.48 (kcal/kg)
Texture	Granular free flowing powder
Color	Black
Odor	Slight

3.1. Characterization of the adsorbent prepared from corncobs

The characteristics of the material prepared from corncob are summarized in Table 1. Moisture, ash, volatile matter and fixed carbon constitute the proximate analysis of charcoal. Fixed carbon represents the percentage of carbon that remains after subtracting the percentage moisture, ash and volatile matter. The total carbon content of the dried adsorbent was 72%. The prepared adsorbent had high moisture content (17%) compared to the raw dried corncobs (3.5%) and ash content was greater than the raw material (1.3%). This can be attributed to the fact that a large amount of volatile matter consisting of steam, gaseous decomposition products was lost. Ash content plays a significant role in the sorption of electrolytes from solution when present in a small quantity [18]. Analysis showed a low sulfur and nitrogen content, i.e. 0.55% and 0.83%, respectively rule out presence of any nitrogen or sulfur based functional group.

Since the material was charred in the presence of air, the functional groups are mainly oxygen containing groups. The FT-IR spectrum (Fig. 1) shows hydroxyl group –OH ($\nu = 3415$ cm^{-1}), carboxyl group–COOH ($\nu = 1697$ cm^{-1}) and COO$^-$ (1616 cm^{-1}). The acidic nature of the aqueous slurry of the corncob carbon shows the presence of these acidic functional groups despite extensive washing. These functional groups can undergo pH dependent coulombic interactions with the sorbate and play important role in the sorption process. The percent ionization of the carboxyl and hydroxyl groups is highly pH dependent owing to the different properties of these groups. The carboxylic acids have a K_a values of about 10^{-5} are sufficiently ionized in the natural pH of slurry (∼3). The negatively charged groups on the adsorbent surface are responsible for electrostatic attractions between the cations and the negative groups. Also the OH groups take part in ion-exchange process, but this should lead to a significant decrease in pH of the solution. However, this was not observed in this study.

The SEM images (Fig. 2) at 600× and 1800× magnification reveal the nature of the surface of the carbonized corncob as a
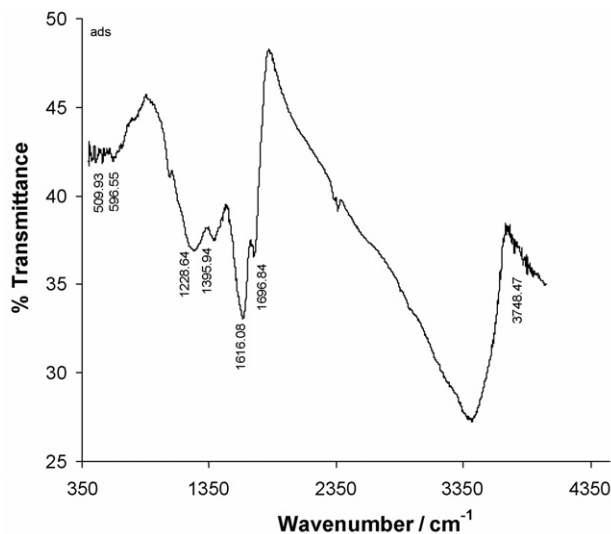
Fig. 1. FT-IR spectrum of the corncob carbon. Possible surface groups on the adsorbent

Peaks (cm^{-1})	Surface groups
3415	ν(O–H)
1697	ν(carboxylic acid –COOH)
1616	ν(ionized carboxyl COO$^-$)

porous reef-like surface and irregular tubular structure, with an average pore diameter of about 39.4 μm.

3.2. pH of point of zero charge

The pH$_{PZC}$ of any adsorbent is a very important characteristic that determines the pH at which the surface has net electrical neutrality. In this work the pH drift method was employed to determine this parameter. It was noted that despite extensive washing of the carbon, the final pH after equilibration decreased rapidly as shown in Fig. 3. At a low pH of 1.92, a slight increase to a pH of 1.94 was observed. The curve obtained cuts the pH$_{initial}$ = pH$_{final}$ line at 2.7. The importance of this value is that
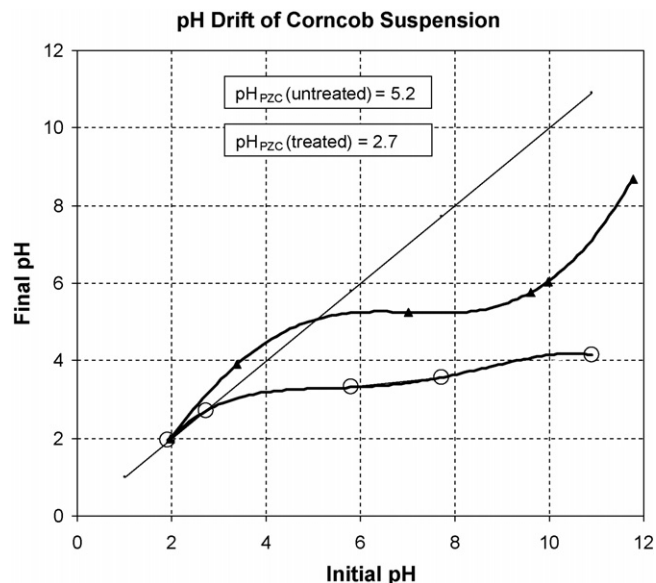

Fig. 3. Suspension test for determining the pH of point of zero charge of corncob carbon by pH drift method. (○) Sulfuric acid treated corncob; (▲) untreated dried corncob powder.

one can readily expect that removal of metal ions is not feasible below this pH because the net positively charged surface is unlikely to attract the cations. This intrinsic acidity of the corncob material is due to the treatment with concentrated sulfuric acid and could not be removed upon thorough washing with distilled water. Since the filtrate of suspension does not give any precipitation with Ba^{2+} (for SO$_4^{2-}$ ions remaining after acid treatment) and silver nitrate (for Cl$^-$ ions), we believe that the acidity is of organic origin.

3.3. Sorption isotherms

The uptake of copper by the prepared activated carbon is shown in Fig. 4. The isotherm illustrates a saturation limit of 4.85 mg copper/g of treated corncob at a pH of 2.4 with an initial copper concentration of 100 mg/L. With a 1000 ppm solution the
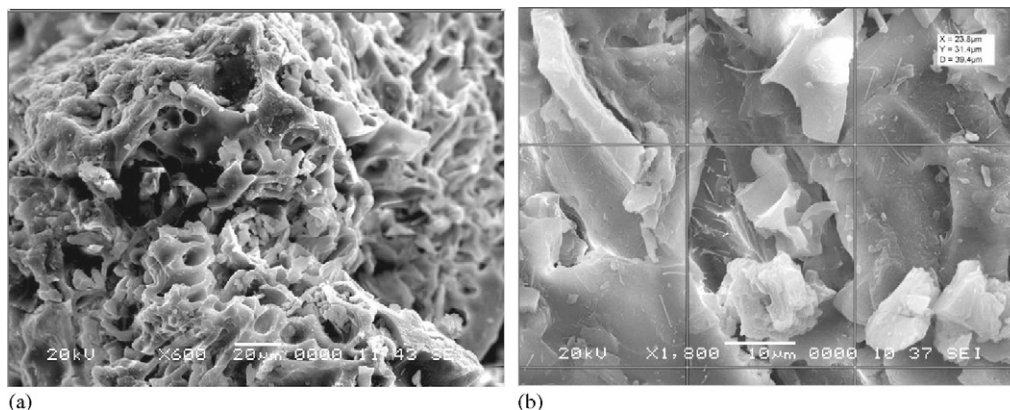

Fig. 2. SEM images of the corncob surface: (a) 600× and (b) 1800× magnification showing the pore structure and pore size.

experimental sorption capacity was 26 mg Cu. Since the q-value was highest for 0.5 g of adsorbent, this amount was chosen for further experiments (Fig. 4).

The equilibrium data was fitted to the Freundlich and Langmuir models:

$$q = KC^{1/n} \quad \text{(Freundlich model)}$$

$$q = \frac{q_m K_a C}{1 + K_a C} \quad \text{(Langmuir model)}$$

where K and n are 0.60 and 1.8, respectively, in the Freundlich model, whereas K_a and q_m are 3.02×10^{-4} and 31.45 for the Langmuir model. Linear plots (R^2-value of 0.9986), of and $1/q$ versus $1/C$ show the applicability of Langmuir isotherm. The maximum sorption capacity value of 31.45 from the Langmuir plot is comparable or better than reported q_{max} value of various commercial carbon prepared from agricultural sources (Table 3). The correlation coefficient obtained with the Freundlich isotherm was 0.9781.

3.4. Effect of pH

The sorption of heavy metals on activated carbon is known to be pH dependent. It was observed by Farajzadeh et al. and Altundogan et al. that the uptake of heavy metals was favored at pH greater than 3.0 because at low values hydrogen ions begin to compete with the metal cation. The pH of point of zero charge measurement on this adsorbent supports this observation, below which the surface is net positively charged and unable to bind Cu^{2+} ions. However, experimental study was necessary to determine the optimum pH of copper removal. Fig. 5 shows the effect of pH on the sorption capacity of the prepared carbon. The highest value was achieved at a pH of 4.5. At this value the dominant specie of copper was free Cu^{2+} ion and mainly involved in sorption process. This has been confirmed by speciation diagram [19] and from absorption spectra. Further experiments at higher values are hindered owing to the immediate precipita-
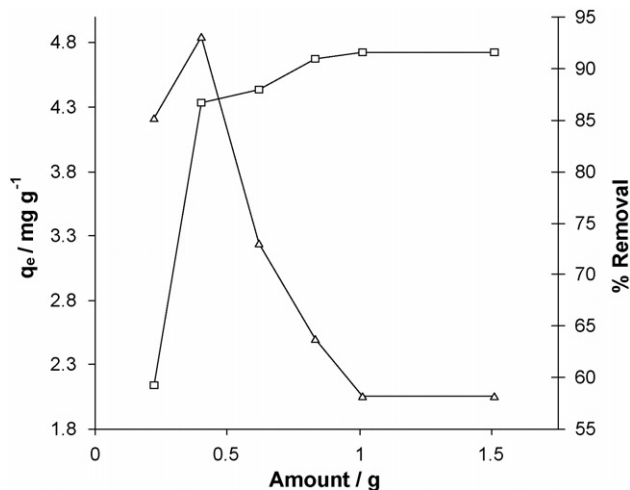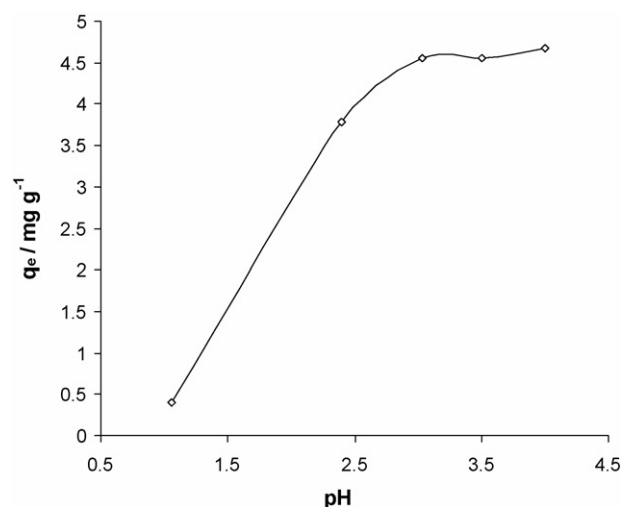
Fig. 5. Effect of pH on the uptake of copper. Amount of adsorbent $= 0.5 \pm 0.01$ g, $[Cu^{2+}] = 50$ mg/L, temperature $= 31.0\,°C$, agitation time $= 2$ min.

tion of blue copper hydroxide. Therefore, to avoid formation of copper hydroxide, we have worked at below pH 4.5. However, Farajzadeh (2003) in his study reported for removal of copper up to pH 10 having very low concentration of copper on rice bran. This was most likely the combined effect of sorption and the formation of precipitation.

3.5. Sorption dynamics

The rate constant k_1 is determined from the following traditional plot for first-order Lagergren rate expression:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where q_t and q_e (mg/g) are the amounts adsorbed at time t (min) and at equilibrium, respectively. A linear relationship was obtained by plotting $\ln(q_e - q_t)$ versus time. This plot revealed that sorption process followed pseudo-first-order kinetics ($R^2 = 0.9917$ and 0.9836 at 304.15 and 318.15 K, respectively). The pseudo-first-order rate constants were found to be $k_1 = 0.1027$ min^{-1} 304.15 K and 0.1778 min^{-1} at 318.15 K, showing that the sorption is very slightly affected by temperature and hence physical adsorption was also involved.

3.6. Competitive removal of copper in binary metal systems

The studies were carried out to investigate the competitive effects in binary Cu–Zn, Cu–Pb and Cu–Ca systems at fixed concentration of copper (100 mg/L) and varying concentration of other metal ions. The pH effect on the metal sorption in mixtures was similar to that in a single-metal system. The competitive effect of the metals was evaluated by comparing the sorption with that in mixtures. Fig. 6 represents the amount adsorbed and percent removal of the copper. Taking into consideration that the Pb^{2+}, Ca^{2+} and Zn^{2+} concentrations were two times higher (200 mg/L) than that of Cu^{2+}, it can be observed that Cu^{2+} removal efficiency was decreased by 53% for Pb^{2+},

Fig. 4. Effect of the dose of adsorbent on removal of copper. $[Cu^{2+}] = 100$ mg/L, temperature $= 31.0\,°C$, agitation time $= 40$ min, pH 2.4. ($\triangle$) q (mg/g); ($\square$) % removal of copper.
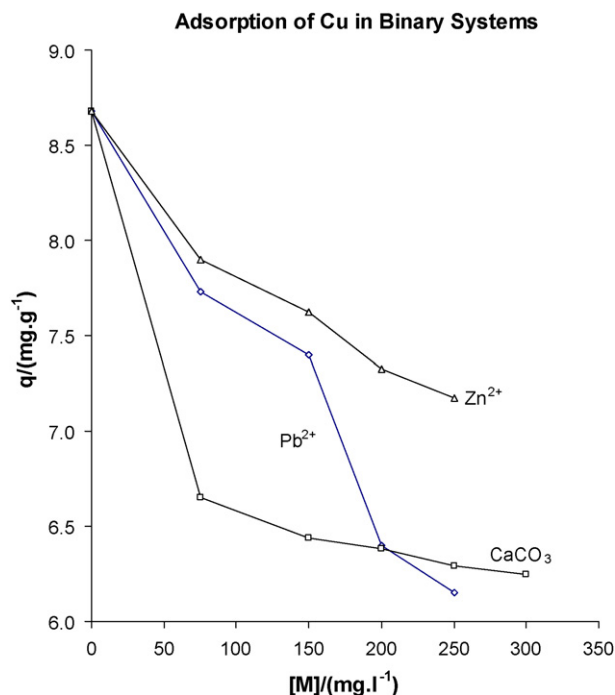
Adsorption of Cu in Binary Systems

Fig. 6. Interference of lead, calcium (water hardness) and zinc on the removal of copper. Initial concentration of $Cu^{2+} = 100$ mg/L, pH 3.0, temperature = $30 \pm 1\,°C$, agitation time = 10 min.

27% for Ca^{2+} and 19% for Zn^{2+}. In all cases, metal sorption onto the adsorbent was found to be competitive in multicomponent systems. The effect of calcium was studied to assess the effect of hard water on the uptake of copper. Toxicity of copper is said to be related to water hardness; according to the Massachusetts Department of Agricultural resources, presence of copper in water with a hardness of less than 20 mg/L $CaCO_3$ is more toxic to fish than copper in the water at a greater hardness [20].

3.7. Removal of anionic and cationic species of copper

Under ordinary conditions copper exists as cupric ions but wastewaters also contain various complexing ions which may bind copper, forming anionic or cationic complexes. This fact has been largely ignored in previous studies [12,21]. This work revealed that the charge on the copper complex played a key role

Table 2
Effect of complexing agents on the adsorption of copper at the optimum pH for complex formation

S. no.	Complex	pH	Cu remaining after adsorption (mg/L)	% Removal
1	$[Cu(H_2O)_6]^{2+}$	3.03	17.25	82.75
2	$[Cu(NH_3)_4]^{2+}$	11.25	0.99	99.19
3	$[Cu(EDTA)]^{2-}$	2.00	100	0
4	$[Cu(EDTA)]^{2-}$	11.32	100	0
5	$[CuCl_4]^{2-}$	<1.00	100	0

Concentration of $Cu^{2+} = 100$ mg/L, agitation time = 10 min, temperature = $30.5\,°C$.

in the sorption process. The removal of only cationic species indicated the nature of surface groups present on the adsorbent (Table 2). At 100 mg/L initial concentration of copper 10-fold excess of complexing agents was added. It was noted that the addition of NH_3 resulted in 99% removal of copper owing to the formation of opposite charged complex specie.
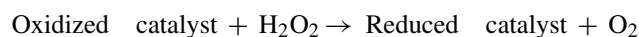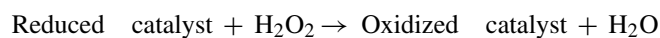
3.8. Regeneration of spent adsorbent

One of the important issues in developing a new adsorbent is its regeneration capability. In this work batch-wise regeneration was carried out. The chemically treated corncobs can be completely regenerated by acidified hydrogen peroxide and it was observed that in four cycles the percentage of removal of copper was greater than 90% in each cycle. The recharging of the spent adsorbent was visible by the blue color of the regenerating solution. The choice of the regenerating solution was totally empirical since hydrogen peroxide has a great tendency to dissolve metallic copper in acidic solutions. Hydrogen peroxide acts as strong oxidizing agent in acidic medium and is

Table 3
Comparison of materials investigated for copper removal

Sorbent	Reported q_{max} (mg Cu/g)
Granulated activated carbon, F-400 [22]	1.89
Rhizopus arrhizus (seaweeds) [22]	15.75
Chlorella vulgaris (seaweeds) [22]	88.2
Pseudomonas aeruginosa (seaweeds) [22]	18.27
Phanerochaete sp. (seaweeds) [22]	26.46
Bone char [11 and references therein]	100
Lignite [11 and references therein]	60
Coal [11 and references therein]	1.62
Carbon prepared from apricot stones [11 and references therein]	12.01
Carbon prepared from coconut shells [11 and references therein]	11.10
Carbon prepared from lignite coal [11 and references therein]	9.80
Carbon prepared from peanut hulls (PHC) [11 and references therein]	89.29
Norit carbon, PK1-3 [11 and references therein]	40
Almond shell carbon [11 and references therein]	2.5
Olive stone carbon [11 and references therein]	6.0
Peach stone carbon [11 and references therein]	3.27
Activated carbons after [11 and references therein]	
(1) Ash discharging	5.0
(2) Followed by oxidation by 13% H_2O_2	9.6
(3) Followed by outgassing at 1400 K in argon atmosphere and contacting with an atmosphere at room temperature	15.3
Commercial activated carbon, India [11 and references therein]	2.74
Zea mays (corncobs) (this study)	26

catalytically decomposed in the presence of heavy metal ions including copper [23]. The general route to decomposition is given by

$$\text{Reduced} \quad \text{catalyst} + H_2O_2 \rightarrow \text{Oxidized} \quad \text{catalyst} + H_2O$$

$$\text{Oxidized} \quad \text{catalyst} + H_2O_2 \rightarrow \text{Reduced} \quad \text{catalyst} + O_2$$

Cu(II)–H_2O_2 system is said to be a Fenton-like reagent and undergoes Cu(II) to Cu(I) cycle while generating free radicals. Since copper is sorbed onto the carbon surface by chemical and physical sorption, it may be possible that these catalytic reactions are responsible for dislodging to copper ions from the loaded material.

In another study by Khan and Zareen [24], they successfully used acidified hydrogen peroxide for regeneration of granite sand loaded with anionic surfactants. The proposed mechanism was also based on free radical generation in the presence of Fe^{2+} ions (Fenton's reagent).

3.9. Application

To check the applicability of the prepared adsorbent, a synthetic sample containing representative 100 mg/L of heavy metals, i.e. nickel, lead, chromium and zinc was prepared. An industrial effluent sample of 500 mL containing 256 mg/L of copper ion was agitated for 40 min at 125 rpm using 5.0 g of the adsorbent. After attainment of equilibrium, sample was analyzed. Result showed that 57% removal of the copper ions took place from the mixture. The same run was also carried out with the two real samples namely A12 and B12, collected from local industrial effluents. The percentage removal of copper was 51.07 and 73.49, respectively. Comparison of other adsorbents studied for copper is summarized in Table 3.

4. Conclusions

Activated carbon was prepared by chemical treatment of corncob by concentrated sulfuric acid. The corncob carbon is prepared from cheap starting materials with low temperature heating without any requirement for a special atmosphere. The corncob carbon can also be recycled by hydrogen peroxide. Also temperature had little effect on the sorption process; this can be important parameter for an adsorbent because the effluents from industries can have higher temperature than the environment. The sorption capacity of the activated carbon was tested on copper removal from aqueous solutions by changing typical adsorption parameters. The maximum sorption was achieved with agitation rate 125 rpm at a solution of pH 4.5 at room temperature. Addition of complexing agents which form negatively charged complexes with copper such as EDTA to the solution completely hindered the sorption of the metal at acidic and alkaline pH. The present study reveals that starting material of the proposed activated carbon is cheap and easily available material. The prepared adsorbent shows an excellent adsorbing capability for copper removal from industrial effluent.

References

[1] J.M. Modak, K.A. Natarajan, An evaluation of copper biosorption by brown seaweed under optimized conditions: a review, Miner. Metall. Proc. 12 (1995) 189–196.
[2] D. Mohan, K.P. Singh, S. Sinha, D. Gosh, Removal of pyridine derivatives from aqueous solution by activated carbons developed from agricultural waste materials, Carbon 43 (2005) 1680–1693.
[3] I. Bodek, W.J. Lyman, W.F. Reehl, D.H. Rosenblatt, Environmental Inorganic Chemistry: Properties, Processes and Estimation Methods, Pergamon, New York, 1998.
[4] Y. Nuhoglu, E. Malkoc, A. Gurses, N. Canpolat, The removal of copper(II) from aqueous solution by Ulothrix zonata, Bioresources Technol. 85 (2002) 331–333.
[5] S.S. Montes, G. Valero, L. Morales, A.M. Vilches, R. Schmidt, Adsorption capacity of copper of natural and modified radiata bark pine, J. Chil. Chem. Soc. 48 (4) (2003) (online version).
[6] A. Shanableh, A. Kharabsheh, Stabilization of Cd, Ni and Pb in soils natural zeolites, J. Hazard. Mater. 45 (1996) 207–217.
[7] P. Zhou, W.F.L. Alfred, W. Shirley, Heavy metal removal from waste water in fluidized bed reactor, Water Res. 33 (8) (1999) 1918–1924.
[8] H.S. Altundogan, F. Tumen, M. Bildik, Arsenic adsorption from aqueous solution by red activated mud, Waste Manage. 22 (2002) 357–363.
[9] K. Kadirvelu, Faur-Brasquest, P. Cloirec, Removal of Cu(II) Pb(II) and Ni(II) by adsorption onto activated carbon cloths, Langmuir 16 (22) (2002) 8404–8409.
[10] R. Pardo-Botello, C. Fernandez-Gouzalez, E. Pinilla-Gil, E.M. Cucrdo-Corrca, V. Gomez-Serrano, Adsorption kinetics of zinc in multicomponent ionic systems, J. Colloid Interf. Sci. 277 (2) (2004) 292–298.
[11] D. Mohan, C.U. Pittman Jr., P.H. Steele, Single, binary and multi-component adsorption of copper and cadmium from aqueous solutions on Kraft lignin—a biosorbent, J. Colloid Interf. Sci. 297 (2006) 489–504.
[12] T. Vaughan, W.S. Chung, E.M. Wayne, Removal of selected metal ions from solution using modified corncobs, Bioresources Technol. 78 (2001) 133–139.
[13] N. Khan, F. Wahab, A simple filtering pipette, Bulgarian J. Chem. Educ. 14 (6) (2005) 520–521.
[14] N. Khan, F. Wahab, A glassware cleaning mixture, Bulgarian J. Chem. Educ. 14 (6) (2005) 518–519.
[15] American Society for Testing Materials, ASTM, 1995, D 3173, D 3174, D 1375, D 24.
[16] Y. Yang, Y. Chun, G. Sheng, M. Huang, pH-Dependence of pesticide adsorption by wheat-residue-derived black carbon, Langmuir 20 (2004) 6736–6741.
[17] Kirk–Othmer Encyclopedia of Chemical Technology, Chapter on Adsorbents, vol. I, 1994.
[18] Cheremisinoff, P.N., Ellerbusch, F., Carbon Adsorption Handbook, Ann Arbor Science, Ann Arbor, MI, 1980.
[19] F.M. Doyle, Z. Liu, The Effect of triethylenetetramine (Trien) on the ion floatation of Cu^{2+} and Ni^{2+}, J. Colloid Interf. Sci. 258 (2003) 396–403.
[20] Massachusetts Department of Agricultural Resources, http://www.mass.gov/agr/pesticides/water/Aquatic/copper.doc (accessed on 9 September 2005).

[21] M.A. Farajzadeh, V.M. Reza, Rice bran as an excellent sorbent for heavy metals from aqueous media. 2. Determination of related parameters, J. Chin. Chem. Soc. 50 (2) (2003) 251–256.

[22] W. M. Antunes, A. S.Luna, C. A. Henriques, C. A. Antonios An evaluation of copper biosorption by a brown seaweed under optimized conditions, Electron. J. Biotechnol. (online) 6 (3) (2003), available at: http://www.ejbiotechnology.info/content/vol6/issue3/index.html.

[23] W.C. Schumb, C.N. Satterfield, R.L. Wentworth, Hydrogen Peroxide ACS Monograph, Reinhold Publishing Inc., New York, 1955.

[24] M. Nasiruddin Khan, U. Zareen, Sand sorption process for the removal of sodium dodecyl sulfate (anionic surfactant) from water, J. Hazard. Mater. 133 (2006) 269–275.