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Removal of Copper(II) and Zinc(II) from Aqueous Solutions Using a Lignocellulosic-Based Polymeric Adsorbent Containing Amidoxime Chelating Functional Groups

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In this study, the adsorption of Cu(II) and Zn(II) ions from aqueous solutions onto amidoximated polymerized banana stem (APBS) has been investigated. Infrared spectroscopy was used to confirm graft copolymer formation and amidoxime functionalization. The different variables affecting the sorption capacity such as pH of the solution, adsorption time, initial metal ion concentration, and temperature have been investigated. The optimum pH for maximum adsorption was 10.5 (99.99%) for Zn^{2+} and 6.0 (99.0%) for Cu^{2+} at an initial concentration of $10\,mg\,L^{-1}$. Equilibrium was achieved approximately within 3 h. The experimental kinetic data were analyzed using pseudo-first-order and pseudo-second-order kinetic models and are well fitted with pseudo- second-order kinetics. The thermodynamic activation parameters such as ΔG^o, ΔH^o, and ΔS^o were determined to predict the nature of adsorption. The temperature dependence indicates an exothermic process. The experimental isotherm data were well fitted to the Langmuir model with maximum adsorption capacities of 42.32 and $85.89\,mg\,g^{-1}$ for Cu(II) and Zn(II), respectively, at 20°C. The adsorption efficiency was tested using industrial effluents. Repeated adsorption/regeneration cycles show the feasibility of the APBS for the removal of Cu(II) and Zn(II) ions from water and industrial effluents.

Keywords adsorption; banana stem; copper(II); graft copolymerization; zinc(II)

INTRODUCTION

The presence of heavy metals in the aquatic environment is one of the major concerns due to their toxicity not only to human beings but also to plants and animals. Heavy metals enter the water bodies through the effluent discharges including electroplating, alloys, fertilizer, pesticides, petroleum oil refineries, mining and battery manufacturing industries and caused a marked increase in concentrations. The removal of heavy metals from water and wastewater has become a very important issue. Numerous studies are being done to develop methods to remove heavy metal ions, particularly from industrial effluents and to subsequently reuse them. Agro wastes have been extensively studied as adsorbents for removing various pollutants from wastewaters and aqueous solutions because of their low cost, biodegradability, sludge form, and availability (1). It has also been observed that these agro wastes need further modifications to increase the active binding sites and also to prevent the leaching of organics such as lignin, tannin, and pectin, which contains polyphenolic, hydroxyl, and carboxylic groups. Chemical modifications such as etherification, graft copolymerization, cross linking, acid and base treatment, and quaternization have been used to improve the chemical and thermal stabilities of the original agricultural residue.

The chemical modification of agricultural residues by graft copolymerization is of great importance because, by grafting of monomers, graft copolymers can be provided new properties such as a hydrophilic or a hydrophobic nature, improved adsorption, and ion exchange capacity. Moreover, graft copolymerization makes it possible to incorporate desired active functional groups on to the backbone of polymers. Graft copolymers incorporated with ethlenediamine, poly(ethyleneimine), amidoxime, acrylamide, dithiocarbamate, polyaniline, and carboxylic acids have been used for the treatment of heavy metal ions (2,3). Adsorbents with amidoxime functional groups are considered as the most promising materials for the recovery of heavy metals from waste water (4). This involves the incorporation of a pendent nitrile group into the polymer matrix through graft polymerization reaction of acrylonitrile onto a polymer substrate, followed by the conversion of the nitrile groups into amidoxime groups by using the alkaline solution of hydroxylamine (5,6).

Banana stem (BS) is an easily available and abundant agricultural waste material. India is the market leader in the production of banana, producing 16,00,000 metric tons annually. BS is largely composed of cellulose, hemicellulose, pectin, tannin, and lignin. This waste creates increasing disposal and potentially severe environmental problems. Any attempt to reutilize this agrowaste will be worthwhile. One of the ways of efficient and environmentally-friendly utilization of biomass waste is its conversion into the adsorbent.

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The utility of this agricultural residue in comparison to other agricultural waste like sawdust, rice husk, bagasse pith, and coconut coir pith is not yet utilized. However, earlier workers have reported the use of BS as a precursor material for the preparation of chelating resins with different functional moieties and successfully employed them as adsorbent for the removal of the same inorganic pollutants from aqueous solutions (7,8,9). In this work, we have focused our attention on the development of an efficient adsorbent from BS for the removal of Cu(II) and Zn(II) from water and wastewater. Since Cu(II) and Zn(II) are of interest to many researchers due to combined environmental and reserve depletion risk factors, adsorption of these metal ions was investigated in this work. In the present work, a new adsorbent, amidoximated polymerized BS (APBS), has been prepared through graft polymerization reaction of acrylonitrile (AN) onto BS using ceric ammonium nitrate (CAN)/nitric acid initiator system, followed by treatment with hydroxylamine hydrochloride and it has been utilized as an adsorbent for the removal and recovery of Cu(II) and Zn(II) from water and wastewater.

EXPERIMENTAL

Materials

The BS (pseudo stem of Musa paradisiaca L) was collected from a local industry. The BS basically contains α-cellulose, hemicelluloses, and lignin which were determined using the standard methods described by Ott (10) and were found to be 61, 18, and 13%, respectively. All chemicals employed in this work were of pure analytical grade and the solutions were prepared with distilled water. The stock solutions of Cu(II) and Zn(II) ions ($1000\,\mathrm{mg\,L^{-1}}$) were prepared by dissolving an appropriate amount of $CuCl_2$ and $ZnCl_2$ (Fluka, Switzerland) in distilled water. The solutions were further diluted to the required concentrations before use. Chloride salts of metals were chosen in the present study because of the dispersion of Cu(II) and Zn(II) into water streams occurs from industries mainly associated with chloride salts. Cupric chloride is extensively used in electroplating, glass, ceramic, mordant, colors, catalyst, manufacturing pesticides and dye industries and various other industrial applications. Zn(II) chloride is commonly used in battery manufacture, petroleum industry, galvanizing, soldering and tanning, and in cooling towers as corrosion inhibitors. The monomer AN obtained from Fluka (Switzerland) was stored at -4°C. Dimethyl formaldehyde (DMF), hydroxylamine hydrochloride, methanol, and CAN were obtained from E. Merck, India limited. 0.1 M NaCl was used to modify the ionic strength in the adsorption experiments. 0.1 M NaOH or HCl were used for pH adjustments. The particle size of the adsorbent was between 80 and 230 US standard mesh (average particle size 0.096 mm).

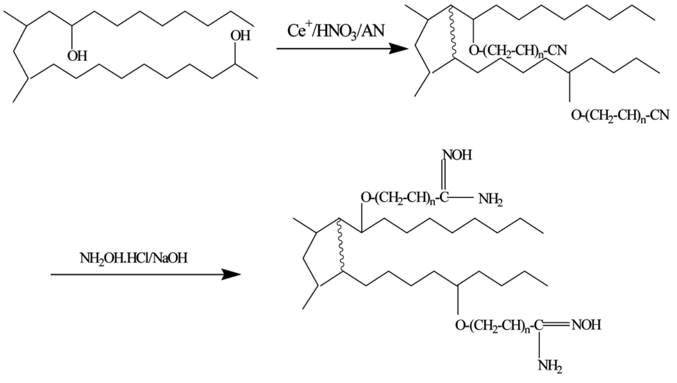
Preparation of Adsorbent

The general procedure adopted for the preparation of the adsorbent is presented in Scheme 1. Twenty grams of dry powdered BS was suspended in 200 ml distilled water in a one liter three neck flask. About 20 ml of diluted HNO_3 (HNO_3:H_2O/1:1) was added to the flask and stirred for 5 minutes and this flask was equipped with a mechanical stirrer, condenser, and a thermometer. About 80 ml of 0.1 M CAN was added to the reaction mixture and allowed to interact for 10 minutes to facilitate free radical formation on the cellulose backbone. The sensitive component for polymer grafting might be the methyl hydroxyl groups of the cellulose unit, BS-CH_2OH. Under controlled supply of nitrogen, 30 ml of AN was added to the suspension. The contents were refluxed for 2 h at 70°C. After the desired reaction time the polyhydroxy grafted product from the reaction mixture was filtered through a sintered glass funnel and was washed with distilled water. The homo polymer of AN (PAN) was highly soluble in water and thus remained in the solution. The grafted product was washed several times with DMF until the weight of the desired product was constant.

About 20 g of the polyacrylonitrile grafted BS (PBS) was socked in 300 ml methanolic solution containing 50 ml of $NH_2OH.HCl$. Then the pH of the solution was adjusted to 10 by using 15.0 N NaOH solution. This was heated for 6 h in a water bath at 70°C. The product, APBS, was filtered and washed with water until the pH of the filtrate was about 7.0 and then dried at 70°C. The adsorbent was sieved and particles having the average diameter 0.096 mm were used throughout the study.

Equipments and Methods of Characterization

The C, H, N, and O contents of BS and APBS were determined with a Carlo Erbo (1801) elemental analyzer. The X-ray diffraction patterns (XRD) of the adsorbents were recorded using a Siemens D 5005 X-ray unit with Ni-filtered Cu Kα radiation. FTIR spectra of the BS and APBS were recorded with a Nicolet Protégé 460 spectrophotometer



SCH. 1. Preparation of APBS.

between 4000 and 450 cm^{-1} using the KBr pellet technique. The methylene blue (MB) adsorption isotherm method was employed to measure the specific surface area of the adsorbents (11). A potentiometric method (12) was used to determine the pH of point of zero charge pH_{pzc}. The surface charge density σ_0 (C cm^{-2}), was calculated from the titration curve using the following equation

$$\sigma_0 = \frac{F(C_A - C_B + [OH^-] - [H^+])}{A} \tag{1}$$

where F is the Faraday constant (C eq^{-1}). C_A and C_B are the concentrations of acid and base (eq l^{-1}) after each addition during titration. $[H^+]$ and $[OH^-]$ are the equilibrium concentration of H^+ and OH^- bound to the suspension surface (eq cm^{-1}). A is the surface area of the suspension ($cm^2 l^{-1}$). A Systronic micro processor pH meter (model 362) was used for pH measurements and a temperature controlled water bath shaker (Labline, India) was used for shaking all the solutions. The concentration of metal solutions was determined using a GBC Avanta A 5450 atomic absorption spectrophotometer (AAS).

Adsorption Studies

Adsorption studies were performed in a 100 mL Erlenmeyer flask with agitation provided by a temperature controlled water bath flask shaker. All adsorption experiments were carried out at room temperature (30°C). The effect of contact time on the adsorption of metal ions onto APBS was done using a batch method. 50 mL of aqueous solutions with various concentrations of metal was placed in a flask containing 0.1 g adsorbent. The flasks were shaken at 200 rpm and at room temperature. The adsorbent was separated from the solution by centrifuging at different time intervals. The concentration of metal in solution was analysed using an atomic absorption spectrophotometer. After kinetic studies, we found that the system reached the equilibrium at 3 h, which was considered different for the removal of metal ions by APBS. The effect of pH on the adsorption capacity was investigated using two different initial metal concentrations of 10 and 25 mg L^{-1} for a pH range of 2.0–6.0 for Cu(II) and 2.0–6.0 and 10.0–12.0 for Zn(II). The initial pH of the Cu(II) and Zn(II) solution in the range 2.0–6.0 was adsorbed using 0.1 M solutions of HCl and NaOH. In order to avoid precipitation in the pH range 10.0–12.0 for Zn(II), pH of the solution was adjusted using 0.1 M HCl and NH_3 solution. Flasks were agitated on a shaker for 3 h. After equilibrium, the concentration of residual metal ions in solution was analysed. Adsorption isotherms were obtained by placing 0.1 g adsorbent on a series of flasks containing 50 mL of metal solutions with various concentrations (10–300 mg L^{-1}). The contents were agitated 200 rpm and at 30°C. After 3 h shaking the adsorbent was separated from the supernatant and the residual metal concentration was determined. The amount of adsorbed metal ions was determined from the difference between the initial and final concentrations of metal ions in equilibrium solution. All adsorption experiments were run in duplicate. The difference in results for the duplicate was less than 4.0%.

Desorption and Reuse Studies

The reusability of the adsorbent was tested by shaking the spent adsorbent in 0.1 M HCl for a period of 3 h. The adsorbent loaded with metal ions was obtained by conducting the adsorption process for 3 h at the desired pH. The adsorbent was separated from the solution by centrifugation and washed gently with water to remove any unadsorbed metal ions. The spent adsorbent was then agitated with 50 ml of 0.1 M HCl, followed by centrifugation for separation. The supernatant solution was analyzed for the desorbed metal ion using AAS. The desorption percentage was calculated using the following equation.

$$\text{Desorption}(\%) = \frac{\text{Amount of metal ions desorbed to the desorption medium}}{\text{Amount of metal ions adsorbed on the adsorbent}} \times 100 \tag{2}$$

The adsorption and desorption processes were repeated for 4 cycles at 30°C.

All the batch experiments were performed in duplicate and the mean values were taken for data analysis.

RESULTS AND DISCUSSION

Adsorbent Characterization

The graft copolymerization reaction was monitored gravimetrically. The percentage grafting efficiency (GE%) was calculated using the following equation:

$$GE_{(\%)} = \frac{W_2 - W_1}{W_3} \times 100 \tag{3}$$

where w_1, w_2, and w_3 are the weights of the BS, APBS, and monomer charged, respectively. The GE was determined to be 78.6%. The amidoxime content (C_{Ao}) in the APBS, in mmol g^{-1} can be determined using the following equation:

$$C_{Ao} = \frac{N_2 - N_1}{14} \times 10 \tag{4}$$

where N_1 and N_2 are the amount of nitrogen (%) in BS and APBS, respectively. The amount of amidoxime groups in the APBS was determined and was found to be 1.57 meq g^{-1}.

The FTIR spectra of BS and APBS shows broad adsorption bands between 3500 and 3300 cm^{-1}, is the characteristic of glucosidic ring of cellulose (Fig. 1). BS shows an absorption peak at 3270 cm^{-1} due to H-bonded O–H stretching vibration and a peak at 2900 cm^{-1} due

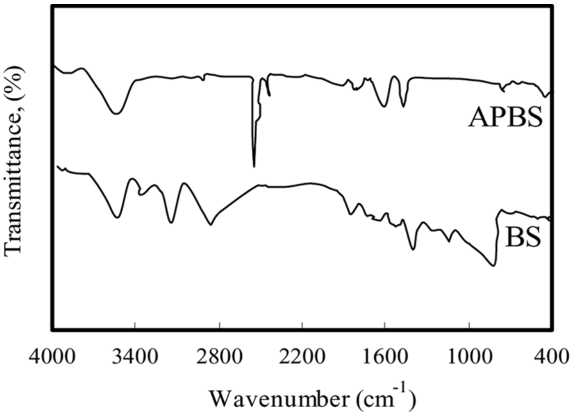


FIG. 1. FTIR spectra of BS and APBS.

to the C-H stretching from $-CH_2$ group. The peaks at 1370 and 896 cm^{-1} in BS are due to the C-O stretching of hemicellulose and glucosidic linkages. The disappearance of peak at 3270 cm^{-1} in the spectrum of APBS indicates the utilization of $-OH$ for grafting. The appearance of a new peak at 1653 cm^{-1} in APBS indicates the presence of an amidoxime group and the peak at 1541 cm^{-1} is due to the presence of $-NH$ stretching vibration of $-NH_2$ group.

The MB adsorption isotherms for BS and APBS were obtained from batch experiments. Isotherm plots (Fig. 2) showed an initial slope and then reached a plateau at equilibrium conditions. The adsorption behavior of MB onto BS and APBS is described as a Langmuir type adsorption isotherm; it indicates that MB was adsorbed onto BS and APBS as a monolayer (Fig. 2). The amount of MB adsorbed as a monolayer can then be related to the specific surface area (SA) by the following equation:

$$S_A = xN_A\sigma \quad (5)$$

where x is the amount of MB adsorbed (mol g^{-1}) when the surface is completely covered with a monolayer of MB, N_A the Avogadro number and σ is the area of the adsorbent covered by one molecule of MB (130 Å^2). Substitution of the value of x obtained from the isotherm plot in the above equation give the value of S_A. The value of S_A was found to be higher for APBS (92.1 $m^2 g^{-1}$) compared to that of BS (53.3 $m^2 g^{-1}$) and due to the enhanced adsorption of MB in the micropores created in APBS, which may provide favorable adsorption sites for MB cations.

The effect of graft copolymerization on the crystallinity of cellulose in BS was studied by the XRD pattern and the results are presented in Fig. 3. The presence of peaks at $2\theta = 22.5$, 22.9, 34.9, and 45.4 indicates a crystalline domain of cellulose structure for BS. The absence of scattering angles at 22.5, 22.9, and 34.9 in APBS, which is present in the original BS, indicates that some rearrangement in the morphology of the cellulose chain occurs as a result of chemical modification. Also, the presence of additional scattering angles at 3.6, 17.1, 28.3, 29.1, and 56.2 in APBS indicates more crystalline domain in it.

The values of pH_{pzc} of the BS and APBS at different ionic strengths (0.001. 0.01, and 0.1 M $NaNO_3$) were determined by a potentiometric titration method and were found to be 8.0 and 4.0, respectively.

Effect of Chemical Modification on Metal Adsorption

For investigating the effect of APBS and BS dosage on adsorption, the experiments were conducted with constant metal ion concentration (25 mg L^{-1}) and samples having different adsorbent dosages ranging from 1 to 7.5 g L^{-1} (solid/liquid). The results of adsorption obtained for metals are given in Fig. 4. For the quantitative removal of 25 mg L^{-1} of Zn^{2+} and Cu^{2+} metal ions a minimum adsorbent dosage of 2.0 and 3.0 g L^{-1} of APBS and 6.5 and 6.0 g L^{-1} of BS were required, respectively. The results clearly indicate that APBS is 3.5 and 2.5 times more effective than BS for the removal of Zn^{2+} and Cu^{2+}, respectively.

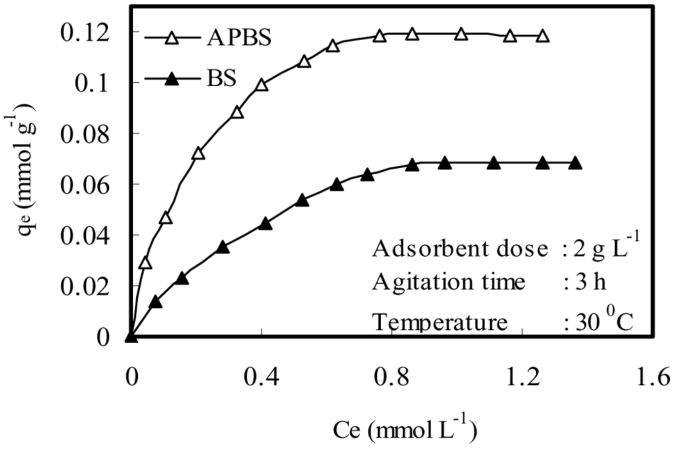


FIG. 2. Adsorption isotherm of MB onto BS and APBS.

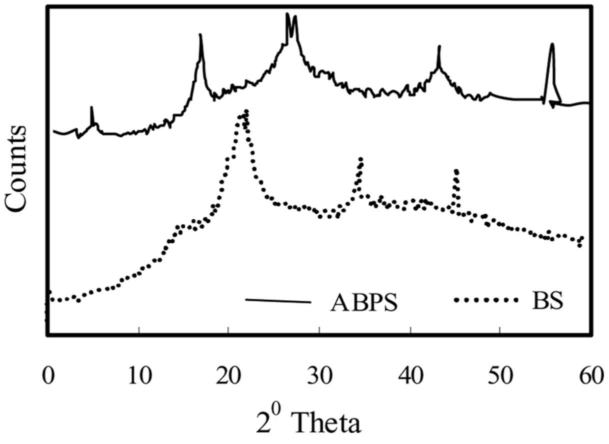


FIG. 3. XRD patterns of BS and APBS.

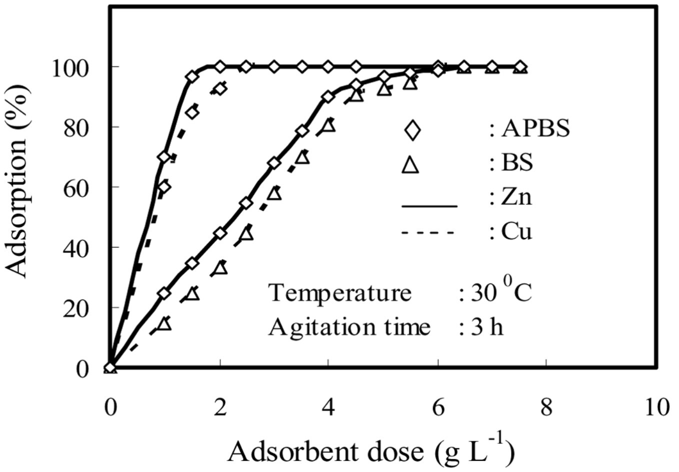


FIG. 4. Effect of adsorbent dose on the adsorption of Cu(II) and Zn(II) on to BS and APBS.

The availability of an increased number of exchangeable sites ensured an enhanced uptake of metal ions. This is a common phenomenon observed when the number of adsorption sites or the active surface area is increased after chemical modification of the original adsorbents (13). The surface area of APBS (92.1 $m^2\,g^{-1}$) is higher than that of BS (53.3 $m^2\,g^{-1}$). The higher metal removal obtained by APBS may be explained by the increase in the crystallanity of APBS, and thereby, the improvement in the access of metal ions to metal binding sites of the adsorbent. The high uptake of APBS may also be caused by $-C(NH2) = NOH$ functional groups formed during amidoximation of BS. The values of pH_{pzc} for BS and APBS were found to be 8.0 and 4.0, respectively. The decrease in the pH_{pzc} after chemical modification indicates that the surface becomes more negative and this also helps to adsorb positively charged metal ions through electrostatic interaction. Since APBS had a higher adsorption efficiency than BS, subsequent adsorption experiments with metal ions were performed only on APBS.

Effect of pH on Cu(II) and Zn(II) Removal

The effect of solution pH on the amount of metal adsorbed was studied by varying the initial pH under constant process parameters at equilibrium conditions. The adsorption data for the uptake of Zn(II) and Cu(II) versus pH at different initial concentrations are shown in Fig. 5. As shown in Fig. 5, the adsorption capacity of metal ions increased with increasing pH of the solution. In highly acidic medium, the adsorption is very low due to the deactivation of the amine sites by protonation. The protonation of amine groups induced an electrostatic repulsion of metal cations and reduced the number of binding sites for metal cations.

In alkaline medium the adsorption of Zn(II) onto APBS is significantly higher and reaches a maximum at pH 10.5. Sorption was not measured in the pH range 6.5–9.5 due to precipitation. The adsorption capacity was observed to be a maximum of 99.8 and 97.9% at an initial concentration of 10 and 25 $mg\,L^{-1}$, respectively at pH 10.5 indicating that $Zn(NH_3)_4^{2+}$ has greater affinity than Zn^{2+}(aq.) on APBS. At pH 10.5 adsorption of Zn(II) on APBS takes place by the complexation mechanism and also by the co-ordination of Zn^{2+} on amine site (14).

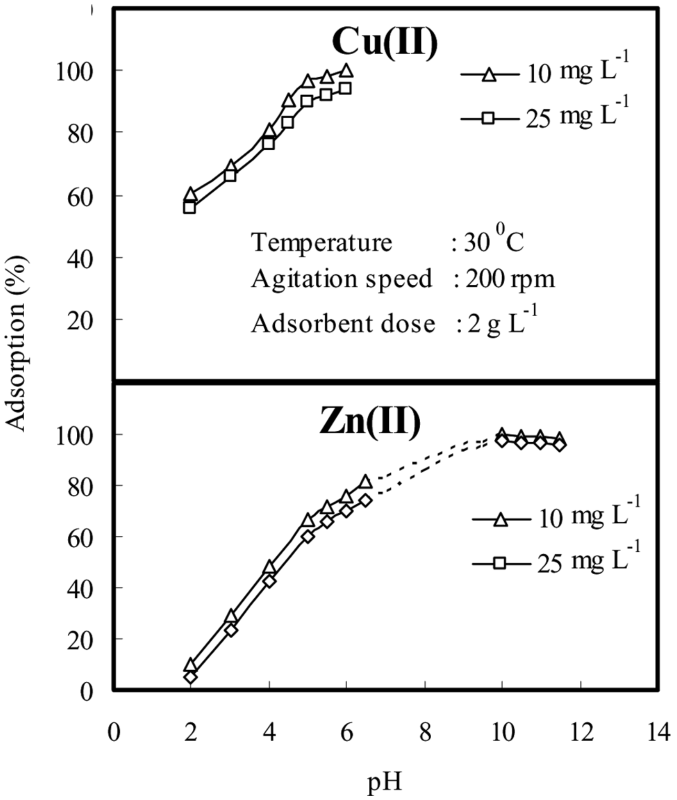


FIG. 5. Effect of pH on the adsorption of Cu(II) and Zn(II) onto APBS.

It has been observed that the final pH is always less than the initial pH. This could be explained by the release of H^+ ions from the surface site of APBS, where Zn^{2+} ions are adsorbed. The sorption decreases only slightly at $pH > 10.0$. The lower basicity of NH_3 as compared to $-C(NH_2) = NOH$ facilitates this reaction.

The adsorption of Cu(II) sharply increases with increasing pH from 2.0 to 4.0, and then remained stable up to 6.0. Sorption was not measured above the pH range 6.0 due to precipitation. Based on the speciation diagrams constructed by Barket (15) and Gibert (16), below pH 7.0 all species of Cu(II) carry a positive charge either as Cu^{2+} or $Cu(OH)^+$. A maximum adsorption of 99.6 and 97.6% occurs at an initial concentration of 10 and 25 $mg\,L^{-1}$, respectively, at pH 6.0. At low pH the competition between H_3O^+ and Cu^{2+} limits the uptake efficiency. At lower pH, the predominant species of Cu(II) is Cu^{2+}, but at higher pH values the hydrolysis products such as $Cu(OH)^+$ is

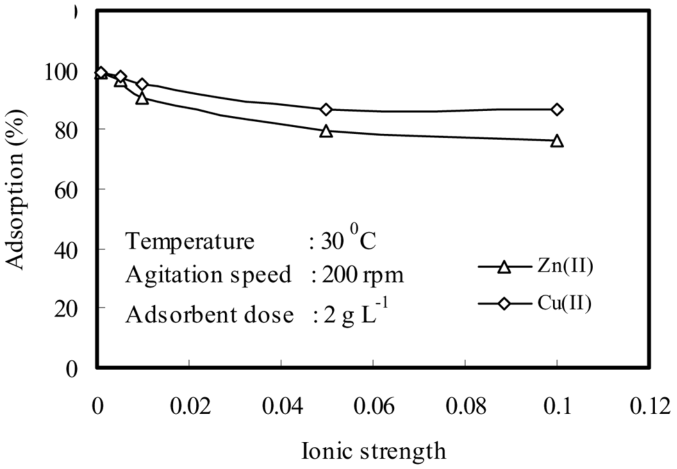


FIG. 6. Effect of ionic strength on the adsorption of Cu(II) and Zn(II) onto APBS.

formed. At the pH range 5.0–6.0, it is believed that ion exchange and complexation processes are major mechanisms for the removal of Cu(II) ions. At pH 6.0, APBS was highly negatively charged ($>pH_{pzc}$) and Cu(II)) ions were positively charged, hence adsorption can be driven by electrostatic attraction between the Cu(II) and the APBS surface. Experimental results show that the final pH is always less than the initial pH.

Effect of Ionic Strength

The effect of ionic strength on the adsorption of Cu (II) and Zn (II) on APBS was studied at 0.001, 0.005, 01, 0.05, and 0.1 M NaCl concentrations at 30°C and an initial concentration of $10\,mg\,L^{-1}$. As seen in Fig. 6, the percentage removal of both Cu(II) and Zn(II) by APBS is decreased with increase in ionic strength. The removal of Cu(II) by adsorption on APBS decreases from 99.3 to 86.5% when the ionic strength increased from 0.001 to 0.1 M; and that of Zn(II) from 99.0 to 76.1%. The adsorption depends on the changes in concentration of the electrolyte if the electrostatic attraction is the significant mechanism for adsorbate removal (17). Also, the results suggest the possibility of ion exchange followed by complexation mechanism for metal adsorption on APBS.

Effect of Initial Concentration and Agitation Period

The removal of Cu(II) and Zn(II) by adsorption onto APBS increases with time and attains a maximum value at 3 h (Figs. 7 and 8). The amount of Cu(II) adsorbed increased from $12.23\,mg\,g^{-1}$ (97.8%) to $33.5\,mg\,g^{-1}$ (67.0%) with an increase in the initial concentration from 25 to $100\,mg\,L^{-1}$. Similarly the amount of Zn(II) adsorbed increased from $12.15\,mg\,g^{-1}$ (97.8%) to $45.8\,mg\,g^{-1}$ (91.6%)

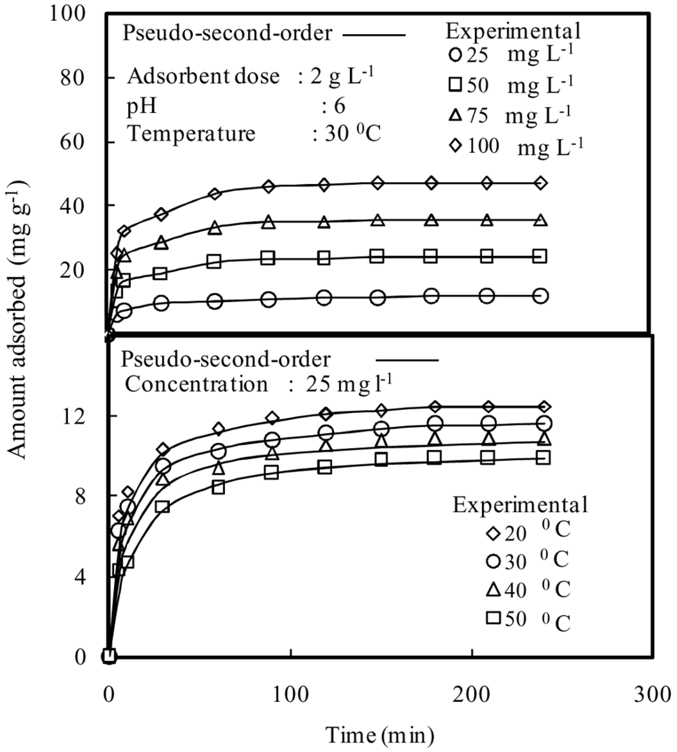


FIG. 7. Effect of initial concentration and temperature on the adsorption of Cu(II) onto APBS.

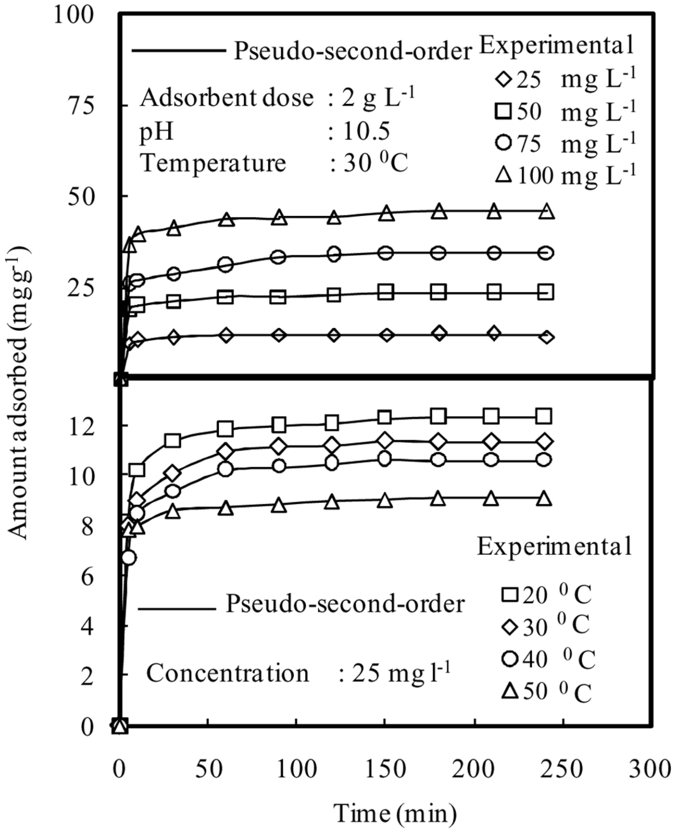


FIG. 8. Effect of initial concentration and temperature on the adsorption of Zn(II) onto APBS.

with an increase in the initial concentration from 25 to 100 mg L^{-1}. This is due to the increase in driving force of the concentration gradient, as an increase in the initial metal concentration. In all the cases, the curves are single, smooth, and continuous, indicating the formation of monolayer coverage of metal ions on the surface of the adsorbent. The curve showed two distinct phases. The first phase is due to the rapid metal uptake and 50–60% adsorption is completed within 15 min, followed by the subsequent adsorption and attains saturation within 3 h. The first phase may be due to the large number of adsorption sites available for adsorption. The second phase is due to the saturation of active sites and attainment of equilibrium. The equilibrium time was found to be independent of initial concentration. Therefore, further studies were carried out using a period of 3 h as a suitable contact time for metal adsorption.

Effect of Temperature

Temperature is an important parameter for any separation process. Studies were carried out to find the effect of temperature in the range of 20–50°C. The initial concentration of metal ions was 25 mg L^{-1}. The results are shown in Figs. 7 and 8. The extent of adsorption of metal ions on APBS was found to decrease with increase in temperature, indicating that, the process is exothermic in nature. With the increase of temperature from 20–50°C the adsorption capacity of Cu(II) decreases from 12.49 mg g^{-1} (99.9%) to 9.86 mg g^{-1} (78.88%) and Zn(II) from 12.46 mg g^{-1} (99.7%) to 11.20 mg g^{-1} (89.65%).

Kinetic Studies of Adsorption

In the present work, the data were analyzed based on pseudo-first-order (18) and pseudo-second-order (19) rate equations, which can be expressed as the following forms:

$$q_t = q_e[1 - e^{(-k_1 t)}] \tag{6}$$

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

where k_1 is the Lagergren rate constant of adsorption (min^{-1}), k_2 is the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}). q_e and q_t are the amounts of metal ion adsorbed (mg g^{-1}) at equilibrium and at time t, respectively. The kinetic parameters for different concentrations and temperatures were determined and are reported in Table 1. All regression constants (R^2) were

TABLE 1
Pseudo-first-order and Pseudo-second-order kinetic parameters for the adsorption of Cu(II) and Zn(II) onto APBS at different initial concentrations and temperatures

		Pseudo-first-order			Pseudo-second-order		
Metal	q_e (exp) (mg g^{-1})	k_1 (min^{-1})	q_e (cal) (mg g^{-1})	R^2	k_2 (min^{-1})	q_e (cal) (mg g^{-1})	R^2
Cu(II)							
Con: (mg l^{-1})							
25	11.58	.025	6.78	0.92	.042	11.62	0.99
50	23.75	.023	12.08	0.89	.018	23.79	0.99
75	35.62	.018	11.85	0.79	.007	35.68	0.99
100	47.00	.012	15.68	0.87	.006	47.06	0.99
Temp: (K)							
293	12.49	.029	6.82	0.91	.045	12.51	0.99
303	11.58	.025	6.78	0.92	.042	11.62	0.99
313	10.85	.023	6.74	0.92	.037	10.89	0.99
323	9.86	.021	6.67	0.95	.028	9.91	0.99
Zn(II)							
Con: (mg l^{-1})							
25	11.49	.023	3.11	0.83	.038	11.52	0.99
50	23.25	.021	7.28	0.89	.012	23.27	0.99
75	34.53	.016	12.87	0.79	.005	34.59	0.99
100	45.80	.009	18.18	0.85	.002	45.87	0.99
Temp: (K)							
293	12.37	.027	3.18	0.86	.040	12.39	0.99
303	11.49	.023	3.11	0.83	.038	11.52	0.99
313	10.63	.021	3.07	0.89	.034	10.64	0.99
323	9.13	.019	3.03	0.81	.022	9.16	0.99

better than 0.99 indicating that the pseudo-second-order kinetic model fitted to the experimental data well. The calculated q_e values from the pseudo-second-order model were also in good agreement with the experimental values (Fig. 7 and 8). These results suggest the adsorption system studied belongs to the pseudo-second-order kinetic model based on the assumption that both ion-exchange and complexation reactions take part in the adsorption process. The values of k decrease with an increase of initial concentration, whereas the values of q_e increase with the increase in initial concentration. The lower the concentration of metal ion in solution, the lower the probability of collisions between these ions, and hence the faster these metal ions could be bonded to the active sites of the adsorbent. In other words, the adsorption rate was inversely proportional to the surface loading. Higher loadings would result in less diffusion efficiency and a higher complexation of metal ions for fixed reaction sites. Similar observations have been made in the adsorption of Zn(II) on amidoximated polyacrylonitrile/bentonite composite (20) and adsorption of Cu(II) on spent activated clay (21).

From the table it is clear that the values of k and q_e decreased with increase of temperature. This indicates the exothermic nature of adsorption. According to the adsorption theory, adsorption decreases with increase in temperature and molecules desorbed from the surface at higher temperatures (22). Also, the rise of temperature affects the solubility and the chemical potential of the adsorbate. If the solubility of the adsorbate increases with an increase in temperature the chemical potential decreases and both the effects, i.e; solubility and temperature effects, work in the same direction, causing a decrease in the adsorption (23).

An Arrhenius plot (ln k vs. $1/T$) was carried out on the experimental kinetic data and from the slope, the activation energy for the process was calculated to be $1.25\,\mathrm{kJ\,mol^{-1}}$ for Cu^{2+} and $1.48\,\mathrm{kJ\,mol^{-1}}$ for Zn^{2+}, indicating that film diffusion might have been the essential rate-limiting step in the adsorption process (24). A process is film diffusion controlled when $Ea < 16.0\,\mathrm{kJ\,mol^{-1}}$. Activation energy value obtained, giving support to the hypothesis that film diffusion is the essential rate-limiting step in the adsorption process.

Other kinetic parameters were calculated using the following Eyring equations (21).

$$\ln k/T = [\ln k_b/h + \Delta s^{\#}/R] - \Delta H^{\#}/RT \qquad (8)$$

where k_b is the Boltzmann constant, h is the Planck constant, T is the absolute temperature, $\Delta S^{o} =$ is the entropy of activation, $\Delta H^{o} =$ is the enthalpy of activation, and R is the gas constant. The plots of ln (k/T) versus 1/T for Cu(II) and Zn(II) were found to be linear (figure not shown). The values of ΔH^{o} and ΔS^{o} were obtained from the slope and intercepts of the plot. The free energy of activation ΔG^{o} can be calculated as $\Delta G^{o} = \Delta H^{o} - T\,\Delta S^{o}$. ΔH^{o} and ΔS^{o} for the adsorption of metal ions were found to be $-13.0\,\mathrm{kJ\,mol^{-1}}$ and $-325.97\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for Cu(II) and $-14.90\,\mathrm{kJ\,mol^{-1}}$ and $-320.89\,\mathrm{J\,mol^{-1}\,K^{-1}}$ for Zn(II), respectively. The negative values of ΔH^{o} suggest the exothermic nature of the process as common for all favorable adsorption process. The higher enthalpic value for Zn(II) gave the higher adsorption capacity than that of Cu(II). The negative values of ΔS^{o} indicate a greater order of reaction during the adsorption. The values of ΔG^{o} were found to be -108.51, -111.77, -115.03 and $-118.28\,\mathrm{kJ\,mol^{-1}}$ for Cu(II) and -79.11, -82.32, -85.53, and $-88.74\,\mathrm{kJ\,mol^{-1}}$ for Zn(II) at 20, 30, 40, and 50°C respectively. The decrease in the value of ΔG^{o}, with the decrease in temperature, demonstrated that the adsorption process was facilitated by the lower temperatures.

Adsorption Isotherm

The adsorptive capacity of APBS for Cu(II) and Zn(II) removal was determined through adsorption isotherm studies. Figure 9 shows the relationship between the quantities

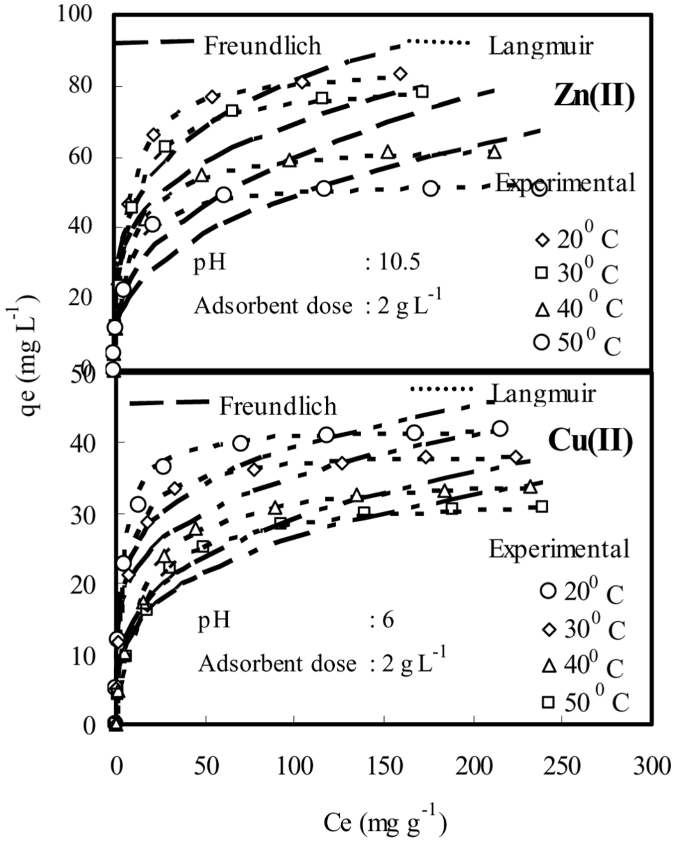


FIG. 9. Experimental and the theoretical curves of Langmuir and Freundlich isotherms in the adsorption of Cu(II) and Zn(II) ions onto APBS.

of metal adsorbed per unit mass of APBS and the equilibrium concentration at 20, 30, 40, and 50°C. All of the isotherms showed similar behavior, and the APBS adsorptive capacity decreased with temperature. As can be seen from Fig. 9, these isotherms can be classified as L-type according to the Giles classification system (26). At higher adsorbate concentrations, a saturation limit is observed, i.e., as C_e approaches infinity, q_e approaches complete monolayer formation. The adsorption isotherms in Fig. 9 tend to define a plateau; therefore, it seems reasonable to suppose that, for the experimental conditions used, the formation of a complete monolayer of metal ions covering the adsorbent is possible and the curves lead to a constant value of q_e. Such a saturation-type curve is defined using the Langmuir equation, which can be represented as (27):

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{9}$$

where q_e is the solid-phase adsorbate concentration at equilibrium ($mg\,g^{-1}$), C_e is the concentration of metal ions in solution ($mg\,L^{-1}$) at equilibrium. The constant q_m gives the theoretical monolayer adsorption capacity ($mg\,g^{-1}$) and b is related to the energy of adsorption.

The other common mathematical model used for describing adsorption isotherm of Zn(II) and Cu(II) on APBS is Freundlich (28) equation, which can be represented as:

$$q_e = K_F C_e^{1/n} \tag{10}$$

where K_F and $1/n$ are Freundlich's constants related to the adsorption capacity and the heterogeneity factor, respectively. The isotherm parameters for different temperatures were determined by non-linear regression analysis using ORIGIN program (version 7.5) and are represented in Table 2.

The Langmuir isotherm parameters were found to be the best fit of the isotherm data in Fig. 9. The correlation coefficient was found to be higher than 0.99. The values of q_m were found to be 42.32, 39, 35.50, and 32.60 $mg\,g^{-1}$ for Cu(II) and 85.89, 81.51, 64.22, and 53.48 $mg\,g^{-1}$ for Zn(II). K_L values were found to be 0.28, 0.18, 0.07, and 0.06 $dm^3\,mg^{-1}$ for Cu(II) and 0.18, 0.16, 0.14, and 0.13 $dm^3\,mg^{-1}$ for Zn(II). The q_m and k_L values decreased with increasing temperature.

The reported q_m values for the adsorption of Cu(II) on sun flower stalk (29) and modified jute fibers (30) were 29.3 and 7.73 $mg\,g^{-1}$, respectively, and for Zn(II) adsorption on sunflower stalk (29), Botrytis Cinerea biomass (31), and modified jute fibers (30), the q_m values were found to be 42.18, 12.98, and 8.02 $mg\,g^{-1}$ respectively. The comparison of q_m values of APBS used in the present study with the literature shows that APBS is more effective for this purpose.

Test with Industrial Wastewater

The utility of APBS has been demonstrated by treating with industrial wastewater. The simulated industrial wastewater of Zn(II) was prepared following the wastewater composition given by Sirianuntapiboom and Hang (32). The Electroplating industrial wastewater sample for Cu(II) was collected from a local industry situated in the industrial belt of Cochin city (India). This wastewater sample was characterized by standard methods (33). The composition of these wastewater samples is given in Table 3. The effect of the adsorbent dose on metal removal by APBS was studied. As seen, metal adsorption generally increases with increasing adsorbent dose. Increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. Figure 10 shows the effect of the adsorbent dose on Cu(II) and Zn(II) adsorption from wastewaters. The complete removal of Cu(II) from wastewater

TABLE 2
Freundlich and Langmuir adsorption parameters for adsorption of Cu(II) and Zn(II) on APBS at different temperatures

		Langmuir				Freundlich			
Metal ions	Temp°C	q_m ($mg\,g^{-1}$)	K_L ($dm^3\,mg^{-1}$)	R^2	χ^2	K_F	1/n	R^2	χ^2
Cu(II)	20	42.32	0.28	0.99	0.66	15.50	0.20	0.92	**13.48**
	30	39.00	0.18	0.99	0.46	12.80	0.21	0.91	**12.34**
	40	35.50	0.07	0.99	0.16	7.60	0.29	0.86	**8.67**
	50	32.69	0.06	0.99	0.53	6.70	0.29	0.91	**7.89**
Zn(II)	**20**	**85.89**	0.18	0.99	**0.85**	**26.43**	**0.25**	**0.94**	**68.22**
	30	**81.51**	0.16	0.99	**0.82**	**23.06**	**0.26**	**0.94**	**56.52**
	40	**64.22**	**0.14**	**0.99**	**0.40**	**17.47**	**0.26**	**0.93**	**42.87**
	50	**53.48**	**0.13**	**0.99**	**0.28**	**15.83**	**0.24**	**0.89**	**45.90**

TABLE 3
Composition of wastewater used for the adsorption of metals onto APBS (mg L^{-1})

Cu(II) (Electroplating industry wastewater)
Cu^{2+}, 43.3; Ni^{2+}, 11.7; Na^{+}, 314.7; Ca^{2+}, 43.4; Mg^{2+}, 611.4; K^{+}, 28.8; Cl^{-}, 319.9; SO_4^{2-}, 29.3; CO_3^{2-}, 89.9; Hardness as $CaCO_3$, 714.4; COD, 413.3; pH, 5.1
Zn(II) (Simulated industry wastewater)
Zn^{2+}, 20.5; Glucose, 1437.5; Urea, 107.3; Ca^{2+}, 24.89; K^{+}, 43.8; Cu^{2+}, 20; $FeSO_4$, 24.8; KH_2PO_4, 43.8; pH, 6.5

sample containing 43.3 mg L^{-1} Cu(II) ions was achieved by 5 g L^{-1} adsorbent dose. Similarly an adsorbent dose of 3 g L^{-1} was required for the complete removal of Zn(II) from wastewater sample containing 20.5 mg L^{-1} Zn(II) ions. To compare the adsorbent efficiency, the effect of the adsorbent dose on metal removal from synthetic wastewater samples (prepared in distilled water) containing only Cu(II) and Zn(II) ions concentrations as similar to wastewater composition, was also studied. An adsorbent dose of 5 and 3 g L^{-1} is required for the complete removal of Cu(II) and Zn(II), respectively. These results are in good agreement with the batch experiments described earlier. Consequently, the present study reveals that APBS is an excellent adsorbent for Zn(II) and Cu(II) removal from wastewaters.

Desorption Studies

To make the adsorption process more economical, it is necessary to regenerate the spent adsorbent and adsorbate. For obtaining the reusability of the APBS the adsorption–desorption cycle was repeated four cycles with the same adsorbent using 0.1 M HCl as the desorbing agent and the results are shown in Fig. 11. After four cycles, the adsorption capacity of APBS declined by 5.3, and 8.5% for Cu(II) and Zn(II), respectively; whereas the desorption of metals decreases from 95.2% for Cu(II) and 97.3% for Zn(II) in the first cycle to 87.6% for Cu(II), and 91.3% for Zn(II) in the fourth cycle. If the adsorbed metal ions on APBS can be desorbed easily by an acid solution, then the adsorption is competing with H^{+} and Cl^{-}. The desorption studies indicate that the mechanism governing the adsorption process cannot be ion exchange alone but may involve complexation through interaction between metals and APBS.

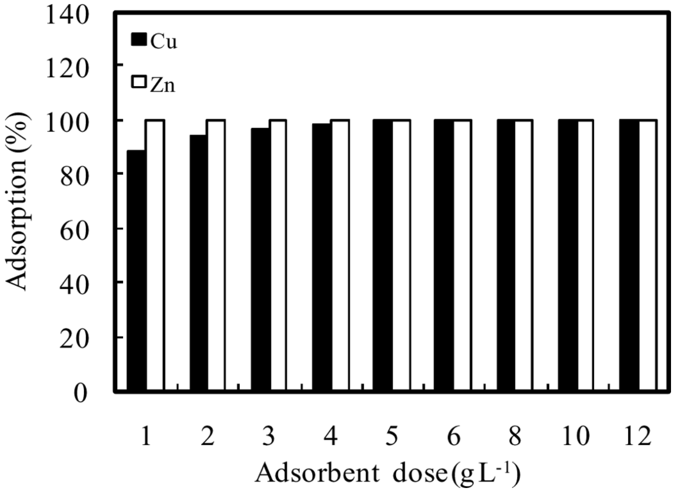


FIG. 10. Effect of adsorbent dose on the adsorption of Zn(II) and Cu(II) from industrial wastewater sample by APBS.

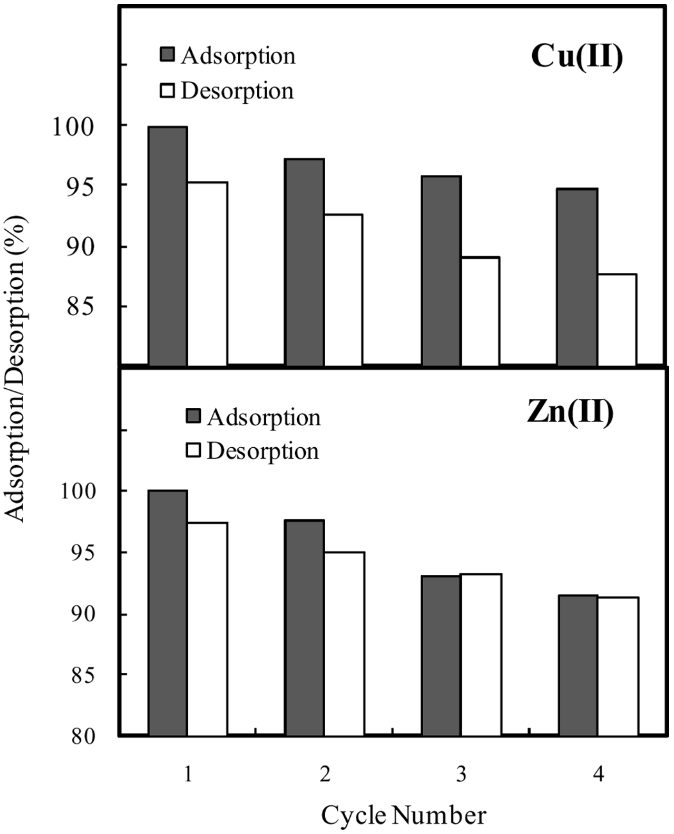


FIG. 11. Four cycles of Cu(II) [A] and Zn(II) [B] adsorption-desorption with 0.1 M HCl.

CONCLUSIONS

In this study, a new adsorbent containing amidoxime groups in graft chain repeating units was prepared and has been successfully used for the removal of Cu(II) and Zn(II) from water and wastewater. The chemical changes observed with FTIR revealed the presence of an amidoxime group. A high adsorption capacity is observed at pH 10.5 for Zn(II); however, the capacity decreases with decrease in solution pH. While the most effective pH range for the removal of Cu(II) was found to be 5.0–6.0, the pseudo-second-order kinetic model gives a better view of the probable rate processes. The isotherm data are better fitted by the Langmuir model as compared to the Freundlich model and the adsorption coefficients agree well with the conditions supporting favorable adsorption. Thermodynamically, the interactions are exothermic followed by a decrease in both Gibbs energy and entropy functions. The utility of the adsorbent was tested using industrial wastewater samples. Regeneration of the spent adsorbent was easily performed with 0.1 M HCl and the adsorbent can be reused for four cycles consecutively.

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REFERENCES

1. Horsfall, Jr.; Abia, M.A.A. (2003) Sorption of Cd(II) and Zn(II) ions from aqueous solutions by cassava waste biomass (Manihot seulenta Cranz). *Water Res.*, 37: 4913.
2. Anirudhan, T.S.; Jalajamony, S.; Suchithra, P.S. (2009) Improved performance of a cellulose based anion exchanger with tertiary functionality for the adsorption of chromium (VI) from aqueous solutions. *Colloids Surf. A: Physichochem. Eng. Aspects.*, 335: 107.
3. Anirudhan, T.S.; Radakrishnan, P.G. (2008) Thermodynamics and kinetics of Cu(II) from aqueous solutions on to a new cation exchanger derived from tamarind fruit shell. *J. Chem. Thermodyn.*, 40: 702.
4. Noriaki, S.; Akio, K.; Masao, T.; Takanobu, S.; Fumio, Y. (2005) Fine fibrous amidoxime adsorbent synthesized by grafting and uranium adsorption-elution cyclic test with seawater. *Sep. Sci. Technol.*, 39: 3753.
5. Pekel, N.; Nurettin, S.; Guven, O. (2000) Development of new chelating hydrogels based on N-vinyl imidazole and acrylonitrile. *Radioactive Phy. Chem.*, 59: 485.
6. Riqueza, E.C.; Aguiar, A.; Maria, L.; Aguiar, M. (2002) Modification of porous copolymers network based on acrylonitrile. *Polym. Bull.*, 48: 407.
7. Noelin, B.F.; Manohar, M.D.; Anirudhan, T.S. (2005) Kinetic and equilibrium modeling of lead(II) adsorption from water and wastewater by polymerized banana stem in a batch reactor. *Sep. Purif. Technol.*, 45: 131.
8. Anirudhan, T.S.; Noelin, B.F.; Manohar, M.D. (2006) Phosphate removal from wastewater using a weak anion exchanger prepared from a lignocellulosic residue. *Environ. Sci. Technol.*, 40: 2740.
9. Anirudhan, T.S.; Senan, P.; Unnithan, M.R. (2007) Sorptive potential of cationic exchange resin of a carboxyl banana stem for mercury (II) from aqueous solutions. *Sep. Purif. Technol.*, 52: 512.
10. Ott, E. (1946) *Cellulose and Cellulose Derivatives*; Interscience Publishers: New York.
11. Viladkar, S.; Agarwal, R.; Kamaludhin, B. (1996) Adsorption of adenine, adenosine and adenosine nucleotides on Nickel (II) hexacyanoferrate (II). *Bull Chem Soc.*, 69: 95.
12. Schwarz, J.A.; Driscoll, C.T.; Bhanot, A.K. (1984) The zero point charge of silica–alumina oxide suspension. *J. Colloid Interf.*, 97: 55.
13. Dadhich, A.S.; Beebi, S.K.; Kavitha, G.V. (2004) Adsorption of Ni(II) using agrowaste, rice husk. *J. Environ. Sci. Eng.*, 46: 179.
14. Manas, C.; Arumugam, P.S. (2005) A novel fibre-coated sorbent for rapid removal of heavy metals from wastewater. Sorption of Zinc (II) from dilute aqueous solutions in the presence of high concentrations of common salts. *Indian J. Chem. Technol.*, 12: 156.
15. Barket, M.A. (2005) Adsorption behavior of copper and cyanide ions at TiO_2-solution Interface. *J. Colloid Interface Sci.*, 291: 345.
16. Gibert, O.; Pablo, J.D.; Cortina, J.L.; Ayora, C. (2005) Sorption studies of Zn(II) and Cu(II) onto vegetal compost used as mixtures for instin treatment of acid mine Drainage. *Water Res.*, 39: 2827.
17. Anirudhan, T.S.; Ramachandran, M. (2006) Adsorptive removal of tannin from aqueous solutions by cationic surfactant-modified bentonite clay. *J. Colloid Interfac Sci.*, 299: 116.
18. Lagergren, S. (1898) Zur theorie der sogenannten adsorption geloster stoffe. *K. Sven. Vetenskapsakad Handl.*, 24: 1.
19. Ho, Y.S.; McKay, G. (2000) The kinetics of sorption of divalent metal ions onto sphagnum moss peat. *Water Res.*, 34: 735.
20. Anirudhan, T.S.; Ramachandran, M. (2008) Synthesis and characterization of amidoximated polyacrylonitrile/organo composites for Cu(II), Zn(II) and Cd(II) adsorption from aqueous solutions and industry wastewaters. *Ind. Eng. Chem Res.*, 47: 6175.
21. Weng, C.; Tsai, C.; Chu, S.; Sherma, Y.C. (2007) Adsorptive characteristics of copper (II) onto spent activated clay. *Sep. Purif. Technol.*, 54: 184.
22. Jnr, M.H.; Spiff, A.I. (2005) Effects of temperature on the sorption of Pb^{2+} and Cd^{2+} from aqueous solution by caladium bicolor (wild cocoyam) biomass. *J. Biotechno.*, 8: 162.
23. Ho, Y.S.; Chiang, C.C. (2001) Sorption studies of acid dye by mixed sorbents. *Adsorption.*, 7: 139.
24. Juang, R.S.; Chen, M.L. (1997) Application of the Elovich equation to the kinetics of metal sorption with solvent impregnated resins. *Ind. Eng. Chem. Res.*, 36: 813.
25. Griffin, R.A.; Jurinak, J.J. (1973) The interaction of phosphate with calcite. *Soil Sci. Soc. Am. J.*, 37: 847.
26. Giles, C.H.; McEwan, T.H.; Nakhwa, S.N.; Smith, D. (1960) Studies in adsorption. Part III. A system of classification of solution adsorption isotherms. *J. Chem. Soc.*, 4: 3973.
27. Langmuir, I. (1918) The Adsorption of gases on plane surface of glass, mica and Platinum. *J. Am. Chem. Soc.*, 40: 1361.
28. Freundlich, H. (1906) Uber die adsorption in losungen. *Z. Phys. Chem.*, 57: 387.
29. Gang, S.; Weixing, S. (1998) Sun flower stalks as adsorbents for the removal of metal ions from wastewater. *Ind. Eng. Chem. Res.*, 37: 1324.
30. Shukla, S.R.; Roshan, P.S. (2005) Removal of Pb (II) from solution using cellulose-containing materials. *Water Res.*, 80: 176.
31. Sibel, T.; Tamer, A. (2006) Zn(II) Biosorption properties of Botrytis Cinera biomass. *J. Haz. Mat.*, 131: 137.
32. Sirianuntapiboom, S.; Hangsrisuwan, T. (2007) Removal of Zn^{2+} and Cu^{2+} by a sequencing batch reactor (SBR) system. *Bioresource Technol.*, 98: 808.
33. APHA. (1992) *Standard Methods for the Examination of Water and Wastewater*, 18th ed.; APHA, AWWA, and WEF: Washington, DC.