

## Preconcentration and determination of Cu (II) from aqueous samples using functionalized sawdust and comparison with synthetic functionalized sorbents

Jasmin Shah<sup>†</sup>, Mohammad Rasul Jan, Maria Sadia, and Atta-ul-Haq

Institute of Chemical Sciences, University of Peshawar, K. P. K., Pakistan  
(Received 2 July 2012 • accepted 5 November 2012)

**Abstract**—The efficiency of indigenous functionalized sorbent (sawdust functionalized with polyaniline) was compared with synthetic functionalized sorbents (Dowex functionalized with 8-hydroxyquinoline (Dowex-8HQ) and  $\alpha$ -nitroso- $\beta$ -naphthol (Dowex- $\alpha$ N/ $\beta$ N)) for preconcentration and determination of Cu (II) from aqueous samples. The synthetic functionalized sorbents and indigenous functionalized sorbent were characterized using FTIR. Different parameters like pH, equilibration time and sample volume were investigated for maximum sorption of Cu (II). Isotherm studies showed that the sorption data fitted well into Langmuir isotherm for the sawdust functionalized with polyaniline. Freundlich isotherm was followed for Dowex-8HQ and Dowex- $\alpha$ N/ $\beta$ N. Four types of kinetic equations were applied to the data, and it was observed that sorption of Cu (II) followed second-order kinetics. Thermodynamically, the sorption of Cu (II) on these three sorbents was found to be exothermic and spontaneous. For maximum recovery of Cu (II) from loaded sorbents, different parameters like shaking time, eluent type, concentration and volume were investigated, and 89% Cu (II) was recovered from loaded sawdust functionalized with polyaniline and Dowex-8HQ. The interference studies showed the selectivity of sawdust functionalized with polyaniline for Cu (II) in comparison to synthetic functionalized sorbents. Thus, Cu (II) can be easily removed from aqueous samples in the presence of foreign ions.

Key words: Sawdust, Polyaniline, Sorption, Preconcentration

### INTRODUCTION

Due to increased industrialization, detoxification by heavy metals has become a well-known problem in recent years, and their occurrence in drinking water is a high risk for humans as well as animals. Heavy metals such as copper, lead, cobalt, cadmium and mercury are non-biodegradable, but can only be diluted or transformed. Thus, the removal of heavy metals is a major task for the industrialists and environmentalists. One of the solutions seems to be their removal before they are being discharged into the aquatic environment [1,2].

Copper is one of the toxic heavy metals causing gastrointestinal problems when taken in excess. The addition of heavy metals in water can be due to natural processes like geological erosion and by the human activities like mining etc. [3]. The main sources of copper in the environment are copper pipes and industrial wastes. The safe limit of copper in drinking water is less than  $4 \mu\text{g mL}^{-1}$  according to the World Health Organization (WHO) [4].

For the determination of heavy metals, some preconcentration or separation step becomes necessary as these are present in the environment at trace level. Preconcentration decreases the limit of detection of heavy metals and also increases the selectivity [5]. Various biological, thermal and chemical methods are available for the determination of heavy metals, including solvent extraction, precipitation, membrane separation, coagulation, ultrafiltration, electrodialysis and adsorption [3]. But the sorption methods including solid phase as extractant are more promising due to simplicity, reus-

ability, environment friendliness, and high preconcentration factor, absence of liquid phase and from economic point of view as well [6,7].

Preconcentration and determination of heavy metals has been done by using unfunctionalized as well as functionalized/modified sorbents which include both biosorbents and ion exchange resins. Biosorbents are cheaper, easily available and their selectivity can be obtained by functionalizing them with some suitable chelating agents. Different functionalized biosorbents such as grains [8], guar gum [9], sugarcane [10], alumina [11] and cotton chelator [12] have been used for the preconcentration and determination of Cu (II), but the most widely used sorbent is modified activated carbon [13] due to the complex formation at the surface between metal ions and acidic functional groups.

Conducting polymers such as polypyrrole and polyaniline can be used for modifying the sorbents due to the ion exchange properties of these polymers. Polyaniline has been used in different applications such as light-emitting diodes, rechargeable batteries, sensors, anti-corrosion coatings and energy storage devices. Polymerization of aniline can be easily done by using any of the oxidizing agents such as potassium or sodium dichromate. Leucoemeraldine, emeraldine base, emeraldine salt and pernigraniline are the four different oxidation states of polyaniline. Among these forms, the most important form of polyaniline is emeraldine base. It is an intermediate form which is 50% oxidized and 50% reduced. Different chemical processes, such as ion exchange, precipitation, complexation and even enzyme reactions, can occur on the polymer surface depending upon the type of acid used, pH range and structure of the polymer [1].

In the present work, indigenous sorbent sawdust has been func-

<sup>†</sup>To whom correspondence should be addressed.  
E-mail: jasminshah2001@yahoo.com

tionalized with polyaniline for preconcentration and determination of Cu (II) in the aqueous samples, thus acting as a cation exchanger. The efficiency of sawdust functionalized with polyaniline was compared with the synthetic functionalized sorbents Dowex-8HQ and Dowex- $\alpha$ N/ $\beta$ N, and it was observed that sawdust functionalized with polyaniline showed greater sorption, higher preconcentration factor and more selectivity for removal of Cu (II) from aqueous samples as compared to synthetic functionalized sorbents Dowex-8HQ and Dowex- $\alpha$ N/ $\beta$ N.

## EXPERIMENTAL

### 1. Instruments

Functionalized sorbents were characterized by using FTIR spectrophotometer Prestige 21 Shimadzu Japan and Quantachrome NOVA 2200e surface area and pore size analyzer. Perkin Elmer AAnalyst 200 Atomic Absorption Spectrophotometer was used for determination of Cu (II).

### 2. Reagents and Solutions

All chemicals and reagents used in this work were of analytical reagent grade purity and purchased from Merck, Darmstadt Germany. These chemicals were used without further purification.

### 3. Solution Preparation

Stock Cu (II) AA standard solution ( $1,000 \mu\text{g mL}^{-1}$ ) was purchased from Merck, Darmstadt Germany. Working standards were prepared from this solution by dilution with distilled water. Britton Robinson Buffer solutions of required pH were prepared according to standard procedure [14] and pH of the solutions was adjusted by adding suitable volume of Britton Robinson buffer.

### 4. Functionalization of Sorbent

Mulberry wood sawdust was collected from a local saw mill and passed through a sieve of 355  $\mu\text{m}$  mesh size. The sawdust was washed with distilled water to remove the dust particles and dried in an oven at  $110^\circ\text{C}$  for 24 hours to constant weight. The dried sawdust was stored at room temperature for further use.

Aniline (10 mL) was added to 100 mL of 2 M hydrochloric acid in a beaker with constant stirring until completely mixed. The mixture was placed in an ice bath and 2 g of washed sawdust was added to it along with dropwise addition of 0.1 M potassium dichromate for 1 h with constant stirring. After polymerization of aniline, the mixture became dark green. The dark green mixture was placed in a refrigerator for about 24 h. Sawdust was then filtered, washed with acetone followed by washing with 2 M hydrochloric acid to remove any unreacted monomer aniline, decomposed products and oxidant. The washed sawdust was finally dried at  $50^\circ\text{C}$  for 48 h and stored for further use as a sorbent.

### 5. Functionalization of Dowex 1X8

Functionalization of Dowex 1X8 with  $\alpha$ -nitroso- $\beta$ -naphthol ( $\alpha$ N/ $\beta$ N) was described previously [15] and the same procedure was used for functionalization with 8-hydroxyquinoline (8HQ).

### 6. Sorption Procedure

For removal of Cu (II) from aqueous samples, different parameters were optimized. For this purpose 100 mg of indigenous and synthetic functionalized sorbents was taken in separate beakers. To each beaker was added 50 mL of  $10 \mu\text{g mL}^{-1}$  of Cu (II) solution. The required pH of each solution was adjusted with the help of pH meter by adding suitable volume of Britton Robinson Buffer. These

mixtures were equilibrated for 60 min at room temperature. The solutions were filtered and Cu (II) was determined in the filtrate by flame atomic absorption spectrophotometer. A sorption isotherms and thermodynamic study was carried out by varying the initial metal ions concentration and temperature from  $25$ – $80^\circ\text{C}$  at optimized conditions.

Sorption capacity ( $q_e$ ) of Cu (II) and % sorption was calculated according to the following general equations:

$$q_e = \left[ \frac{C_i - C_f}{m} \right] V \quad (1)$$

$$\% \text{ sorption} = \left[ \frac{C_i - C_f}{C_i} \right] \times 100 \quad (2)$$

Where  $q_e$  is the amount of Cu (II) sorbed on the sorbent ( $\text{mg g}^{-1}$ ),  $C_i$  and  $C_f$  are the initial and equilibrium concentrations of Cu (II) in  $\mu\text{g mL}^{-1}$ , respectively;  $V$  is the volume of Cu (II) solution in mL and  $m$  is the amount of sorbent in g. Desorption study was carried out using nitric acid and hydrochloric acids in different molar concentrations.

## RESULTS AND DISCUSSION

### 1. Characterization of the Sorbents

To confirm the successful functionalization of sawdust, FTIR spectra of unfunctionalized and functionalized sawdust were recorded and are shown in Fig. 1. On comparing the spectra, it was observed that in case of modified sawdust, new IR bands have appeared. These bands are at  $1,127 \text{ cm}^{-1}$  for C-H stretching,  $1,383 \text{ cm}^{-1}$  for C=N stretching and at  $3,410 \text{ cm}^{-1}$  for N-H stretching. Thus, FTIR analysis indicated the successful functionalization of sawdust with polyaniline.

The surface area of the unwashed sawdust and sawdust functionalized with polyaniline was measured using nitrogen sorption with Quantachrome Surface Area Pore Size Analyzer (NOVA 2200e). The specific surface area was calculated using BET, Dubinin-Radushkevich (DR) and BJH isotherm equations. The micropore volume of the sorbent was calculated by DR plot and BJH equation using the NOVA Win2 data analysis software, and average pore width

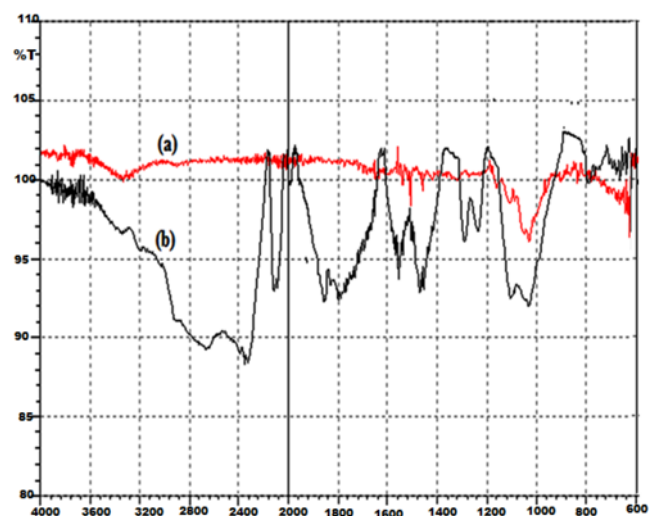
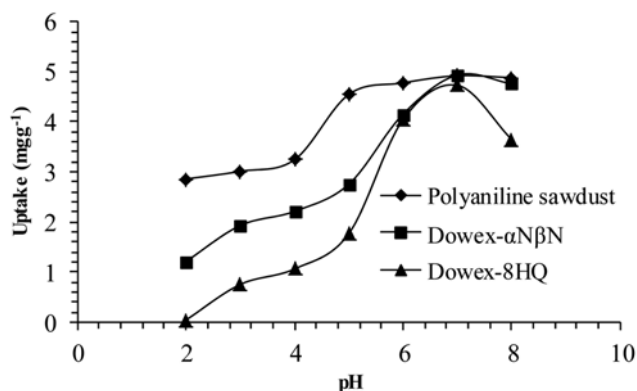


Fig. 1. Comparison of FTIR spectra of unfunctionalized (a) and functionalized (b) sawdust.

**Table 1. Characteristics of unwashed, washed and functionalized sawdust**

Sawdust	Surface area (m <sup>2</sup> g <sup>-1</sup> ) by different methods			Average pore width (Å)		Micropore volume (ccg <sup>-1</sup> )	
	BET	DR plot	BJH method	DR plot	BJH method	DR plot	BJH method
Unwashed sawdust	46.87	115.07	81.48	143.73	99.38	0.04	0.16
HCl washed sawdust	60.54	142.21	106.83	144.88	118.40	0.05	0.31
Sawdust functionalized with polyaniline	84.60	202.63	131.31	132.00	123.79	0.07	0.39

**Fig. 2. Effect of pH on uptake of Cu (II) from aqueous solution using functionalized sawdust, Dowex-αNβN and Dowex-8HQ.**

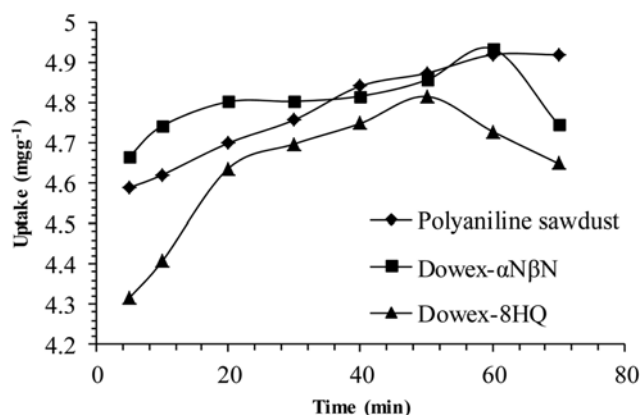
was calculated using DR plot and BJH equation and the results are given in Table 1. These results show that the surface area and micropore volume of sawdust has been increased by modification.

## 2. pH Effect

The solution pH is an important factor which affects the sorption phenomenon. To investigate the effect of pH on sorption of Cu (II), pH of the solution was varied from 2.0 to 8.0 using Britton Robinson buffer (Fig. 2). For sawdust functionalized with polyaniline, maximum sorption of Cu (II), 98.4% was observed at pH 7 due to formation of undoped form of polyaniline polymer with availability of free groups of imine or amine for metal chelation. At lower pH, sorption was less, which may be due to change of polyaniline into acidic form that protonated the imine and amine, thus showing that polyaniline polymer cannot act as a chelating agent. As pH of the solution was increased, sorption of Cu (II) decreased, which could be due to the formation of hydroxide of the metal ions. For Dowex-8HQ and Dowex-αNβN, maximum sorption of 94.6% and 88.7% was observed at pH 7. At lower pH sorption was less for Cu (II) due to the presence of higher concentration of H<sup>+</sup> ions which may be competing with Cu (II) for the sorption sites. At higher pH decrease in sorption using Dowex-8HQ may be due to formation of metal hydroxides and limited availability of metal ion in free form for complex formation.

## 3. Effect of Equilibration Time

The effect of contact time on sorption of Cu (II) was investigated in the range of 5 to 70 min (Fig. 3). The process of sorption is faster in the beginning due to the availability of sorption sites on the sorbents, but with the passage of time, as these sorption sites become occupied with the metal ions, the sorption process becomes slow. The sorption of Cu (II) on sawdust functionalized with polyaniline increased from 91.8% to 98.4% in 40 min, whereas for Dowex-

**Fig. 3. Effect of contact time on uptake of Cu (II) from aqueous solution using functionalized sawdust, Dowex-αNβN and Dowex-8HQ.**

8HQ and Dowex-αNβN, the maximum sorption was observed at 50 min and 60 min, respectively. These results show that rate of sorption of Cu (II) is faster for sawdust functionalized with polyaniline as compared to Dowex-8HQ and Dowex-αNβN.

## 4. Kinetic Studies

The sorption data obtained from equilibration time study of Cu (II) were fitted in four common kinetic equations like pseudo-first-order, pseudo-second-order, intraparticle diffusion and Elovich equations. The model for pseudo-first-order is expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303} \quad (3)$$

Where  $q_e$  is the amount of metal ion sorbed (mg g<sup>-1</sup>) at equilibrium,  $q_t$  is the amount of metal ions sorbed (mg g<sup>-1</sup>) at any given time (min) and  $K_1$  is the pseudo-first-order reaction rate constant for sorption (min<sup>-1</sup>). The values of constants  $K_1$ ,  $q_e$ ,  $R^2$  were calculated from the slope and intercept of linear line of first-order kinetics and are given in Table 2.

The model for pseudo-second-order is as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2} \quad (4)$$

Where  $q_e$  is the amount of metal ion sorbed (mg g<sup>-1</sup>) at equilibrium,  $q_t$  is the amount of metal ions sorbed (mg g<sup>-1</sup>) at any given time (min) and  $K_2$  is the pseudo-second-order reaction rate constant for sorption (g mg<sup>-1</sup> min<sup>-1</sup>). The values of constants  $K_2$ ,  $q_e$  and  $R^2$  were calculated from the slope and intercept of linear line of second order kinetics and are given in Table 2.

For all three sorbents, the value of sorption capacity calculated from second-order kinetics is closer to the experimental value, and

**Table 2. Kinetic parameters for sorption of Cu (II) from aqueous solution**

Sorbent	$q_e$ (mg g <sup>-1</sup> ) (exp)	Pseudo first order kinetic model			Pseudo second order kinetic mode			Intra particle diffusion model			Elovich model		
		$K_1$ (min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$	$K_2$ (gm g <sup>-1</sup> min <sup>-1</sup> )	$q_e$ (mg g <sup>-1</sup> )	$R^2$	$K_{int}$ (mg g <sup>-1</sup> min <sup>1/2</sup> )	C	$R^2$	$\alpha$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$\beta$ (g mg <sup>-1</sup> )	$R^2$
Polyaniline sawdust	4.92	1.80	0.62	0.0577	0.33	4.93	0.9998	0.06	4.44	0.9853	5.8E+12	7.25	0.9496
Dowex- $\alpha$ N $\beta$ N	2.22	0.05	0.45	0.1763	0.07	2.32	0.9825	0.12	1.16	0.9307	7.44	3.54	0.8756
Dowex-8HQ	4.82	1.09	2.32	0.1045	1.09	4.73	0.9993	0.06	4.26	0.6879	5.19E+9	5.93	0.8083

also the correlation coefficient values for the pseudo-second-order are higher as compared to first-order model. The data shows that the sorption of Cu (II) might be controlled by pseudo-second-order kinetics for all three sorbents.

Intraparticle diffusion is a kinetic model related to the transfer of sorbate ions from its aqueous media to the pores of sorbent. This model is generally expressed by the following equation:

$$q_t = K_{int} t^{1/2} + C \quad (5)$$

Where C is the intercept and related to the thickness of the boundary layer and  $K_{int}$  (mg g<sup>-1</sup> min<sup>-1/2</sup>) is the intraparticle diffusion rate constant. The values of these constants were calculated directly from the intercept and slope of the linear form (Table 2). The plot of  $q_t$  versus  $t^{1/2}$  does not pass through the origin, which indicates that intraparticle diffusion is not only the controlling step during sorption of Cu (II) on these three sorbents but some other mechanisms are also involved.

The Elovich kinetic equation is used to describe the kinetics of chemisorption on heterogeneous surfaces and is given as follows:

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (6)$$

Where  $q_t$  is the amount of Cu (II) sorbed (mg g<sup>-1</sup>) at time (t),  $\alpha$  and  $\beta$  are known as the Elovich coefficients,  $\alpha$  represents the initial sorption rate (mg g<sup>-1</sup> min<sup>-1</sup>), and  $\beta$  is related to the extent of surface coverage and activation energy for chemisorption (g min<sup>-1</sup>), respectively. The Elovich coefficients were calculated from the linear plot of  $q_t$  versus  $\ln t$  (Table 2). On comparison of  $\alpha$  value, it can be concluded that the initial rate of sorption of Cu (II) is highest for sawdust functionalized with polyaniline followed by its sorption on Dowex-8HQ and in the case of Dowex- $\alpha$ N $\beta$ N; initially the process of sorption is very slow. The value of  $\beta$  is also greater for sawdust functionalized with polyaniline.

### 5. Sorption Isotherm Study

The sorption data for all three sorbents was fitted into the two most common isotherms, Langmuir and Freundlich, in order to evaluate the nature and mechanism of sorption of Cu (II). The linear form of Freundlich equation is given below:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (7)$$

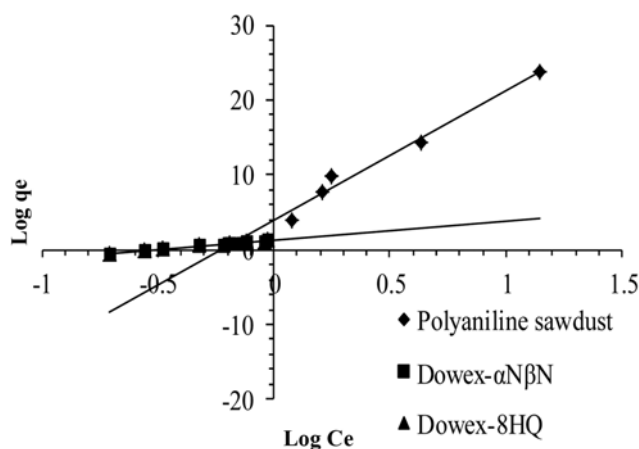
Where  $K_F$  is the Freundlich sorption isotherm constant (mg g<sup>-1</sup>),  $q_e$  is the amount sorbed in mg g<sup>-1</sup> and  $C_e$  is the equilibrium concentration in  $\mu$ g mL<sup>-1</sup>.  $1/n$  (g L<sup>-1</sup>) is a measure of the sorption intensity,  $n$  is the measure of the deviation from linearity of sorption. Its value

indicates the degree of non-linearity, as if the value of  $n$  is equal to unity, the sorption is linear; if the value is below to unity, this indicates that sorption is chemical; if the value of  $n$  is above to unity sorption is a favorable physical process.

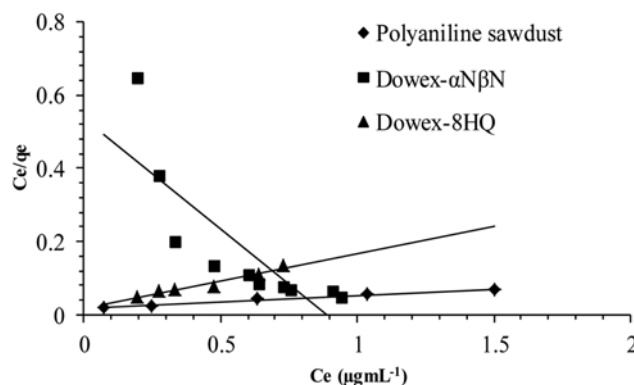
In a linear form, the Langmuir isotherm is expressed as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L} \quad (8)$$

Where  $C_e$  is the equilibrium concentration in  $\mu$ g mL<sup>-1</sup>,  $q_e$  is the amount of solute adsorbed per gram of sorbent,  $K_L$  and  $a_L$  are the Langmuir



**Fig. 4. Freundlich isotherm model for sorption of Cu (II) from aqueous solution using functionalized sawdust, Dowex- $\alpha$ N $\beta$ N and Dowex-8HQ.**



**Fig. 5. Langmuir isotherm model for sorption of Cu (II) from aqueous solution using functionalized sawdust, Dowex- $\alpha$ N $\beta$ N and Dowex-8HQ.**

**Table 3. Freundlich and Langmuir parameters for sorption of Cu (II)**

Type of sorption isotherm	Parameters		
	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N
Freundlich isotherm			
n (Lg <sup>-1</sup> )	1.57	0.39	0.39
K <sub>F</sub> (mgg <sup>-1</sup> )	21.19	21.40	21.40
R <sup>2</sup>	0.98	0.99	0.99
Langmuir isotherm			
Q <sub>o</sub> (mgg <sup>-1</sup> )	28.73	6.68	1.65
a <sub>L</sub> (Lmg <sup>-1</sup> )	0.62	8.23 × 10 <sup>3</sup>	1.13 × 10 <sup>3</sup>
R <sup>2</sup>	0.98	0.96	0.67

**Table 4. Thermodynamic parameters for sorption of Cu (II) using polyaniline sawdust, Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N as sorbents**

T (K)	$\Delta G^\circ$ (KJmol <sup>-1</sup> )			$\Delta H^\circ$ (KJmol <sup>-1</sup> )			$\Delta S^\circ$ (JK <sup>-1</sup> mol <sup>-1</sup> )		
	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N
298	-152.38	-64.85	-188.11						
313	-129.50	-49.24	-63.78						
323	-128.96	-41.78	-49.56						
333	-123.65	-35.37	-40.08	-10.81	-299.18	-20.10	6.64	66.80	39.75
343	-101.23	-33.52	-37.43						
353	-90.535	-18.52	-29.24						

adsorption isotherm constants and are related to the maximum capacity (Lg<sup>-1</sup>) and bonding strength (Lmg<sup>-1</sup>), respectively. The theoretical monolayer sorption capacity is Q<sub>o</sub> and is numerically equal to K<sub>L</sub> a<sub>L</sub><sup>-1</sup>.

The linear forms of Freundlich and Langmuir isotherms are shown in Figs. 4 and 5, respectively. The values of different constant parameters calculated from the slope and intercept of linear form of Freundlich and Langmuir isotherms are given in Table 3. It can be seen from the table that the value of n is greater than unity for sawdust functionalized with polyaniline whereas for Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N is less than unity employing that sorption of Cu (II) on sawdust functionalized with polyaniline is linear, whereas sorption of Cu (II) on Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N is non-linear. For Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N, the sorption capacity calculated from the Freundlich isotherm and also the R<sup>2</sup> values are greater as compared to the Langmuir isotherm, indicating that sorption of Cu (II) is following the Freundlich isotherm on these two sorbents. The sorption capacity calculated from the Langmuir isotherm is higher for sawdust functionalized with polyaniline as compared to the Freundlich isotherm, and the sorption data of Cu (II) is best fitted to the Langmuir isotherm.

## 6. Thermodynamic Studies

Thermodynamic studies were performed by studying the temperature effect on sorption of Cu (II) on the three sorbents, and different thermodynamic parameters were determined using the van't Hoff equation which is expressed as follows:

$$\ln K_D = -\frac{\Delta G^\circ}{RT} = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (9)$$

Where K<sub>D</sub> is the distribution constant,  $\Delta G^\circ$  is Gibbs free energy,

$\Delta H^\circ$  is change in enthalpy and  $\Delta S^\circ$  is change in entropy.  $\Delta G^\circ$  and K<sub>D</sub> can be calculated using the following equations.

$$\Delta G^\circ = -RT \ln K_D \quad (10)$$

$$K_D = \frac{q_e}{C_e} \quad (11)$$

Where q<sub>e</sub> is the amount of metal ions sorbed (mgg<sup>-1</sup>) at equilibrium and C<sub>e</sub> is the equilibrium concentration in  $\mu$ gmL<sup>-1</sup>.

The values of ln K<sub>D</sub> and 1/T were calculated and a plot between ln K<sub>D</sub> against 1/T was drawn.

The values of  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated using above equations and are given in Table 4. The negative value of  $\Delta H^\circ$  shows that the sorption of Cu (II) on all three sorbents is exothermic with greater enthalpy changes in case of Dowex-8HQ, and least in case of sawdust functionalized with polyaniline. The negative value of  $\Delta G^\circ$  shows spontaneity of sorption process on all the three sorbents, and the positive value of  $\Delta S^\circ$  shows strong affinity of sorbent for sorption of Cu (II), which is highest for Dowex-8HQ.

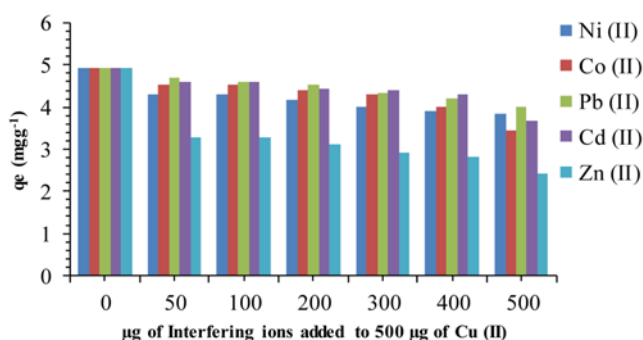
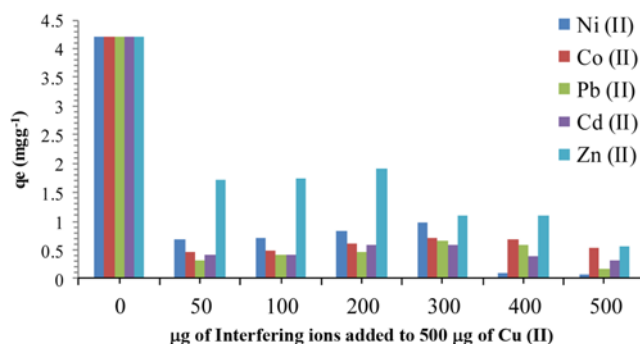
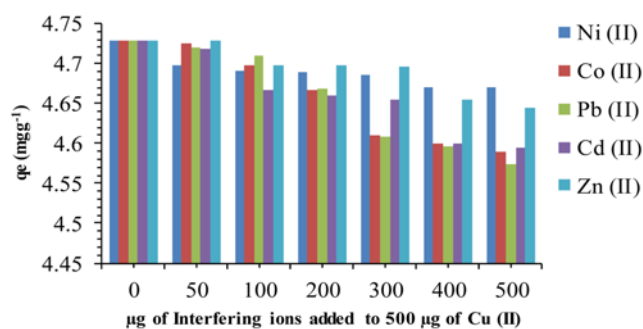
A comparison of Cu (II) sorption studied on sawdust functionalized with polyaniline at optimum conditions is compared with some of the sorbents used in the literature (see Table 5). As can be seen, the efficiency of the studied sorbent is comparable with the reported sorbents in terms of % sorption, but the sorption process on the studied sorbent is exothermic and therefore requires minimum time for sorption.

## 7. Interference Study

The selectivity of the functionalized sorbents was evaluated by studying the effect of selected foreign ions. Their effect was studied in the range of 50 to 500  $\mu$ g under optimum conditions on sorption capacity of the sorbents for the target metal ion. The results are shown

**Table 5. Comparison of sorption efficiency of studied sorbent with sorbents in literature for Cu(II) sorption**

Type of sorbent	Sorption (%) of Cu (II)	Optimum contact time (h)	Desorption (%) of Cu (II)	Langmuir sorption capacity (mg/g)	Nature of sorption process	References
Present work (Sawdust with polyaniline)	98.40	0.40	89.76	28.73	Exothermic	
Bentonite embedded in the polyacrylamide	97.00	---	20.00	33.00	Endothermic	16
Chitosan grafted onto the surfaces of MWCNTs	95.00	---	---	---	---	17
$\beta$ -Cyclodextrin modified multiwall carbon nanotube	99.00	20.00	---	---	Endothermic	18
Multiwalled carbon nanotubes in the absence and presence of humic acid (HA) or fulvic acids (FA)	90.00	---	---	5.52 with HA and 5.54 with FA	Endothermic	19
Elais Guineensis Kernel Activated Carbon	---	---	100	---	---	20
Activated carbon prepared from pomegranate peel	---	2.00	100	21.98	---	21

**Fig. 6. Effect of interfering ions on sorption capacity of Cu (II) using functionalized sawdust.****Fig. 8. Effect of interfering ions on sorption capacity of Cu (II) using Dowex-αN/βN.****Fig. 7. Effect of interfering ions on sorption capacity of Cu (II) using Dowex-8HQ.**

in Figs. 6-8 for sawdust functionalized with polyaniline, Dowex-8HQ and Dowex-αN/βN, respectively. It can be seen from the figure that the sorption capacity of modified sawdust is not being affected by the foreign metal ions investigated except Zn (II). Whereas for Dowex-8HQ, at higher concentration of interfering ions, the sorption capacity decreases especially with Co (II), Pb (II) and Cd (II) beyond 100 µg concentration. For Dowex-αN/βN, all the ions show

interferences even at smaller concentrations. Thus, the interference study suggests that functionalized sawdust could be selectively used for the sorption of Cu (II) in the presence of Ni (II), Co (II), Pb (II) and Cd (II) as compared to Dowex-8HQ and Dowex-αN/βN.

### 8. Desorption Studies

Desorption of the sorbed metal ions is very important not only for preconcentration and subsequent determination of metal ion at trace level, but also for the reuse of the sorbent to minimize solid waste. In case of sawdust functionalized with polyaniline, the imine groups in polyaniline become protonated in acidic solution and desorption leads to the removal of metal ions. In case of Dowex-8HQ and Dowex-αN/βN, since the maximum sorption of Cu (II) occurs at higher pH, for desorption various concentration of hydrochloric acid (0.5 to 6.0 M) and nitric acid (0.5 to 2.0 M) were tried and the amount of desorbed Cu (II) was determined by FAAS. The results are shown in Fig. 9. The maximum desorption (89.76%) was observed with 10 mL of 0.5 M HNO<sub>3</sub> for sawdust functionalized with polyaniline, while in case of Dowex-8HQ and Dowex-αN/βN, maximum desorption 89.46% and 59.86% was observed with 20 mL of 6.0 M HCl and 1.0 M HNO<sub>3</sub> respectively.

The effects of shaking time on desorption of Cu (II) from func-

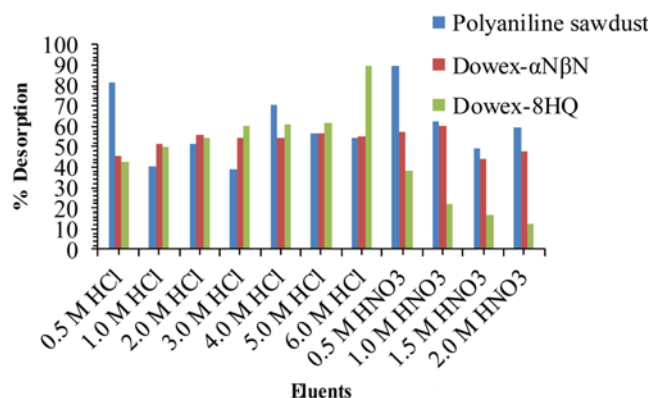


Fig. 9. Effect of type of eluent on % desorption of Cu (II) from functionalized sawdust, Dowex- $\alpha$ N $\beta$ N and Dowex-8HQ.

tionalized sorbents were also investigated, and the optimum shaking time for desorption of Cu (II) from modified sawdust was found 10 min, whereas for Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N, the optimum shaking time was 60 min and 70 min, respectively. This shows that Cu (II) is strongly chelated with the synthetic functionalized sorbents as compared to indigenous functionalized sorbent from which it can be easily recovered.

The effect of eluent volume on % desorption was also investigated. The eluent volume was varied from 5 to 25 mL, and it was observed that 10 mL was the optimum eluent volume for maximum desorption of Cu (II) from sawdust functionalized with polyaniline, whereas 20 mL was the optimum eluent volume for Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N.

#### 9. Effect of Sample Volume on % Sorption and Preconcentration Factor

For finding the effect of sample volume, the total metal ion concentration (500  $\mu$ g) and the amount of sorbents (100 mg) were kept constant and the sample volume was varied from 50 to 1,000 mL. For sawdust functionalized with polyaniline and Dowex-8HQ, there is no prominent effect of increasing sample volume on % sorption of Cu (II) as its sorption decreases from 100.0% to 80.5% with increasing sample volume from 50 mL to 1,000 mL. Whereas in case of Dowex- $\alpha$ N $\beta$ N, sorption of Cu (II) decreases to 4.9% when sample volume is increased up to 1,000 mL.

The preconcentration factor was calculated and is given in Table 6. A maximum preconcentration factor of 100 was obtained for sawdust functionalized with polyaniline with maximum recovery.

#### 10. Application of Functionalized Sorbents for Preconcentration and Determination of Cu (II)

The sorbent modified for preconcentration of Cu (II) was applied

Table 6. Preconcentration factor for Cu (II) from functionalized sawdust, Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N

Initial sample volume (mL)	Final eluent volume (mL)			Preconcentration factor		
	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N	Polyaniline sawdust	Dowex-8HQ	Dowex- $\alpha$ N $\beta$ N
50	10	20	20	5	2.5	2.5
100	10	20	20	10	5.0	5.0
150	10	20	20	15	7.5	7.5
200	10	20	20	20	10	10
300	10	20	20	30	15	15
400	10	20	20	40	20	20
500	10	20	20	50	25	25
1000	10	20	20	100	50	50

Table 7. Real sample application for the preconcentration and determination of Cu (II) using polyaniline sawdust, Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N as sorbents

Spiked aqueous samples	$\mu\text{g mL}^{-1}$ added	$\mu\text{g mL}^{-1}$ found			Sorption (%)			Desorption (%)		
		Polyaniline sawdust	Dowex- 8HQ	Dowex- $\alpha\text{N}\beta\text{N}$	Polyaniline sawdust	Dowex- 8HQ	Dowex- $\alpha\text{N}\beta\text{N}$	Polyaniline sawdust	Dowex- 8HQ	Dowex- $\alpha\text{N}\beta\text{N}$
River Jhelum										
	3	2.97±0.19	2.97±0.10	2.88±0.26	97.62±0.08	97.6±0.08	71.90±0.24	99.06±0.41	90.06±0.41	58.90±0.38
	5	5.21±0.17	5.21±0.17	4.98±0.26	96.90±0.24	95.9±0.24	60.80±0.20	88.63±0.19	88.63±0.19	55.00±0.19
	7	7.39±0.23	7.39±0.09	6.98±0.15	97.00±0.10	94.0±0.10	59.00±0.45	88.04±0.41	78.04±0.41	51.90±0.68
Tube well										
	3	3.00±0.24	3.00±0.04	3.08±0.16	98.27±0.71	98.2±0.71	73.9±0.29	92.19±0.17	89.1±0.17	53.90±0.56
	5	5.13±0.45	5.13±0.10	4.88±0.09	98.58±0.27	95.5±0.27	62.4±0.72	89.82±0.14	89.8±0.14	50.00±0.43
	7	6.97±0.34	6.97±0.13	6.99±0.10	98.44±0.16	93.4±0.16	55.5±0.40	87.54±0.19	77.5±0.19	59.50±0.67
Tap water										
	3	2.97±0.18	2.97±0.04	2.88±0.26	96.55±0.28	96.5±0.28	72.9±0.18	95.27±0.40	89.2±0.40	52.00±0.25
	5	4.87±0.27	4.87±0.14	4.98±0.26	97.82±0.22	96.8±0.22	61.9±0.24	88.92±0.14	88.9±0.14	58.90±0.38
	7	6.96±0.35	6.96±0.04	6.68±0.29	97.30±0.56	92.3±0.56	50.8±0.20	87.06±0.45	75.0±0.45	55.00±0.19



for the determination of Cu (II) in different water samples collected from laboratory tap, tube well and river Jhelum. As there was no Cu (II) in these water samples, therefore all samples were spiked with known concentration of Cu (II) by standard addition method and their sorption and desorption was studied at optimum conditions. The results are given in Table 7 for sawdust functionalized with polyaniline, Dowex-8HQ and Dowex- $\alpha$ N $\beta$ N. The water samples were spiked with different concentrations (3.0 to 7.0  $\mu\text{g mL}^{-1}$ ) of Cu (II), and their concentration was determined by FAAS. Sorption of Cu (II) for different spiked samples is in the range of 96.5 to 98.5% with desorption ranging from 87.0 to 99.0% for sawdust functionalized with polyaniline. % sorption of Cu (II) was from 92 to 98%, and maximum desorption (75.0 to 90.0%) was observed for Cu (II) in case of Dowex-8HQ, whereas for Dowex- $\alpha$ N $\beta$ N, sorption of Cu (II) from aqueous samples was in the range of 50.8 to 71.9% with desorption of 51.9 to 58.9%. The results indicated that the sawdust functionalized with polyaniline could be effectively used for preconcentration and determination of Cu (II) in real samples at trace level. This sorbent could also be used for the removal of Cu (II) from aqueous samples.

## CONCLUSION

The sorption study revealed that sawdust functionalized with polyaniline as a sorbent material was suitable for preconcentration and removal of Cu (II) as compared to commercially available synthetic resins which were functionalized with chelating groups. The sorption data of Cu (II) on functionalized sawdust fitted well into the Langmuir isotherm with the sorption capacity ( $Q_m$ ) of 28.73  $\text{mg g}^{-1}$ . Sawdust is low cost and environmentally friendly, and after functionalization high sorption uptake and regeneration make it a suitable sorbent for the removal and preconcentration of Cu (II) from aqueous samples.

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