Pak. j. sci. ind. res. Ser. A: phys. sci. 2017 **60**(3) 128-133

Efficiency for Sorption Behaviour of Polymeric Resins of (2-hydroxybenzaldehyde) with Aliphatic and Aromatic Diamines Towards Different Metal Ions

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(received April 29, 2017; revised August 23, 2017; accepted August 28, 2017)

Abstract. Aliphatic and aromatic polymeric resins of (2-hydroxybenzaldehyde) with 1,2-propylenediamine and 1,4-phenylenediamine were synthesised and characterised employing elemental and thermal analysis, FT-IR and UV-visible spectroscopy. The metal uptake behaviour of synthesised polymers (PMBHBPn, PMBHBPh) towards different metal ions were investigated and optimised by variety of conditions. The sorption data of these metal ions were followed Langmuir, Freundlich, and Dubinin-Radushkevich (D-R) isotherms. The Freundlich parameters were computed at $1/n$ = 0.26 ± 0.02, 0.309 ± 0.02, 0.35 ± 0.05, 0.368 ± 0.04 and 0.23 ± 0.01, A = 3.9 ± 0.03, 4.31 ± 0.02, 4.683 ± 0.01, 5.43 ± 0.03, and 2.81 ± 0.05 mmol/g for Cu(II), Co(II), Ni(II), Fe(III) and Cd(II) ions, respectively. The variation of sorption with temperature gives thermodynamic quantity (ΔH) in the range of (AH = 36.33 - 52.14 KJ/mol) for (PMBHBPn) and (39.21-56.29 KJ/mol) for (PMBHBPh). The sorption procedure could preconcentrate metal ions, and it can be determined by atomic absorption spectrophotometer.

Keywords: polymeric resin, sorption, isotherms, kinetics, thermodynamics

Introduction

The metals have high density as compared to water (Bradl, 2002). The bulkiness and toxicity are interconnected with heavy metals including metalloids at low level of exposure (He *et al*., 2005). In recent times, there are rising ecological and global public health issues related to environmental toxicity by heavy metals. Similarly, human exposures are also rising dramatically as a result of their numerous uses in industrial, agricultural, domestic and technological activities (Harvey and Mcardle, 2008). However, the sources of heavy metals in the surroundings included geogenic, industrial, agricultural, pharmaceutical and domestic effluents and atmospheric sources are affecting all the living species (Wang and Shi, 2001). Different industrial processes are the main source of environmental pollutions (Beyersmann and Hartmig, 2008) and (Atsdr, 2002). Hence, heavy metals are also known as toxic metals even at lower concentrations (ppb range to less than 10 ppm) in different environmental samples.

Copper is an essential element for all living organisms because it is a key constituent for proper growth and health. In humans, copper is mostly existing in the liver, muscle, and bones (WHO, 1996). The mature body contains 1.4-2.1 mg of copper per kg of body weight. The precision quantities of nickel and cobalt have also been revealed to be essential for healthy life, such as level of nickel should not be exceeded to 5 ppm in drinking water (Sari *et al*., 2007; Xie *et al*., 2005). Cobalt is one of the essential elements for life but chronic cobalt intake has caused serious health problems (Kocaoba, 2008; Akl *et al*., 2004). The estimated value for soluble cobalt salts is 150-500 mg/kg. Iron is an essential mineral found in every cell of the body because it is needed to make hemoglobin, a part of blood cells (Blain and Traguer, 1995).

Chelating resins are designed as useful sorbent resins for determining concentration of metal ions from different environmental samples (Bortoleto *et al*., 2004; Saracoglu and Elci, 2002). Different polymeric resins indicated the equilibrium of adsorption method and also compared with different adsorption isotherm equations like Sips, Langmuir, Freundlich, and linear adsorption isotherms (Fafy *et al*., 2010; Xiaojun *et al*., 2010). Ortho hydroxyl derivatives also indicated positive ability to form the metal complexes with Schiff base polymers (Samal *et al*., 1997; 1996). This research describes the

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synthesis of polymeric Schiff base of 2-hydroxy benzaldehyde with aliphatic diamine (1,2-propylenediamine) and aromatic diamine (1,4-phenylenediamine) by polycondensation reaction and utilized as adsorbent (resins) for Cu(II), Co(II), Ni(II), Fe(III) and Cd(II) ions. The preconcentration was followed in this sorption method and the concentrations were determined by atomic absorption spectrophotometer.

Materials and Methods

Reagents and materials. All chemicals were of analytical grade. 2-hydroxybenzaldehyde, 1,2-propylenediamine, 1,4-phenylenediamine, formaldehyde, organic solvents (ethanol, methanol, *n*-hexane), HCl, KCl, acetic acid, sodium acetate, ammonia and NH_4Cl solutions were required and purchased from Merck/Germany.

Instruments. FT-IR spectrophotometer and thermal analyzer were the two main instruments used in this study. FTIR-spectrum was recorded on Nicolet Avatar 330 FT-IR with total attenuated reflectance (ATR) accessory. Spectrophotometric studies were carried out in tetrahydrofuran (THF) using double beam Hitachi 220 spectrophotometer (Hitachi (Pvt) Tokyo, Japan). Thermogravimetry (TG) was recorded on Pyris Diamond TG/DTA (Perkin Elmer, Japan) from room temperature to 550 °C against α-alumina as reference.

Preparation of resin. The Schiff base polymers of 2-hydroxybenzaldehyde with aliphatic and aromatic diamines were prepared by reported procedure (Samal, 1997) with some modifications.

Schiff base (1.2 g) of (2-hydroxybenzaldehyde) was dissolved in 20 mL distilled water and added about 10-12 drops of 2M NaOH. The mixture was slightly heated at 50 °C for 10 min, during that time formaldehyde (37% v/v, 2.4 mL) also added with continuous stirring on hot plate. The mixture was refluxed for 2.5 h at 120 °C. After refluxing, poured the mixture, filtered the precipitates and washed with hot water. Melting point of resin was higher than 300 °C. Structure diagram of polymers is shown in Fig. 1(a-b). Elemental analysis of polymeric resins is as follows:

1. Poly (5,5′-methylene bis(2-hydroxy benzaldehyde)1,2-propylenediimine) $(C_{18}H_{21}N_2O_2)n$, Calculated C, 76.83 %; H, 4.87 %; N, 8.53 %. Found C, 76.66 %; H, 4.89 %; N, 8.51%.
2. Poly (5,5′-methylene bis(2-hydroxy benzaldehyde)1,4-phenylenediimine) Elemental $(C_{21}H_{19}N_2O_2)n$, calculated: C, 76.83 %; H, 4.87 %; N, 8.53 %. Found: C, 76.66 %; H, 4.89 %; N, 8.51

Sorption process. ***Preparation of solution by batch method.*** Polymers (PMBHBPn & PMBHBPh) (0.1 g) were treated with aqueous solution of 0.05 M Cu (II) Co(II), Ni(II), Fe(III) and Cd(II) metal ions of known concentration (10 mL, 2000 μg/mL). The pH of solution was maintained with buffer. The concentrations of unknown solutions were determined by atomic absorption spectrophotometerically. After knowing the concentration of solutions, maximum percentage of sorption and the distribution co-efficient (Kd) were calculated from following equations.

$$\% \text{ Sorption} = Ci - Cf/Ci \times 100 \quad \text{......................... (1)}$$

Ci = Initial concentration of metal ions in solution (mg/L)
Cf = Final concentration of metal ions in solution (mg/L).

$$Kd = \frac{\text{mmol metal ion in resin}}{\text{mmol metal ion in the solution}} \times \text{......... (2)}$$

$$\frac{\text{volume of solution (mL)}}{\text{weight of resin (g)}}$$

All thermodynamic parameters like ΔH, ΔG and ΔS were obtained from the following relationships:

$$\log K_c = \frac{-\Delta H\ RT}{2.303} + \frac{\Delta\ R}{2.303} \quad \text{............................ (3)}$$

$$\Delta G = -RT \ln K_c \quad \text{.. (4)}$$

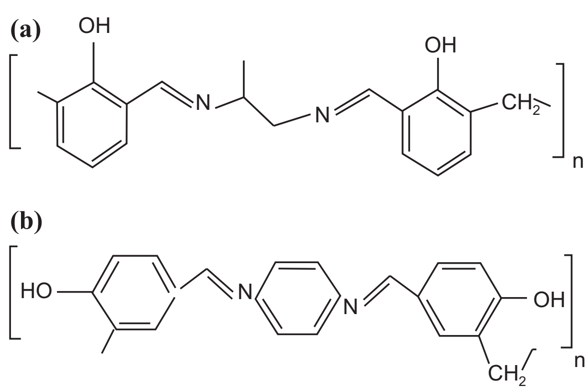


Fig. 1(a-b). Structural diagram of Ploy[5,5′-methylenebis (2-hydroxybenzaldehyde)1,2-propylenediimine].

Results and Discussion

Characterisation of resins. The FTIR spectrum of polymers (PMBHBPn and PMBHBPh) showed all main characterisation peaks such as C=N stretching vibration at 1636.62 and 1648.34 cm^{-1}, the main O-H band appeared at 1258 and 1265 cm^{-1} and C=C bands at 1533-1618 cm^{-1}, respectively in Fig. 2(a-b).

The data of ultra violet - visible spectrum of polymeric resins (PMBHBPn) and (PMBHBPh) show three absorption bands at 248-253 nm (1% ε = 463-457 L g/cm), 282-296 nm (1% ε =275.4- 266.3 L/g/cm), and 342- 346 nm (1% ε =205.8- 207.5 L/g/cm), respectively (Fig. 3a-b).

Thermal stability of polymeric resins was observed on thermogravimetry thermal analyzer and it gives two mass loss steps from room temperature to 550 °C, (Fig. 4). This suggested that the maximum mass loss is 76% at about 422 °C which referred the rigidity of polymeric resin.

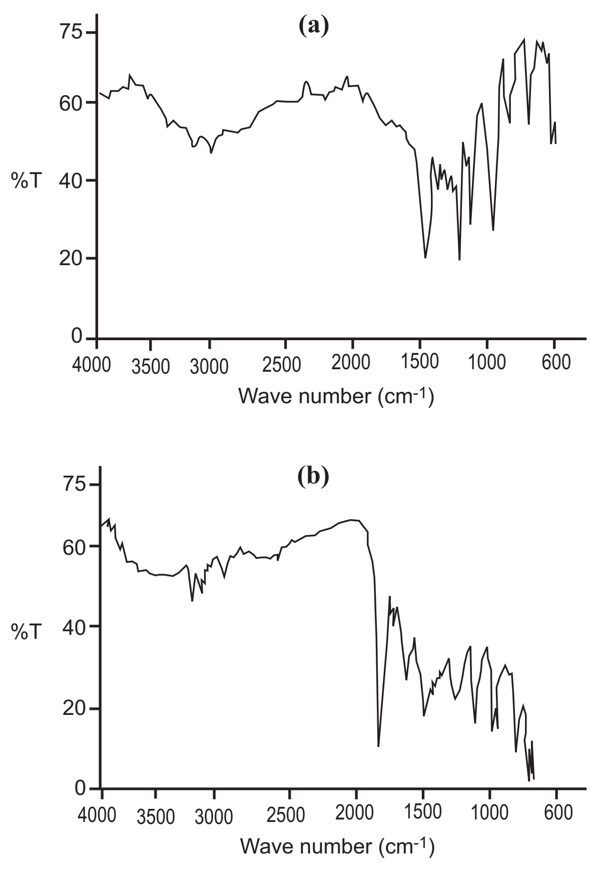


Fig. 2(a-b). FTIR spectra of (a) (PMBHBPn) (b) (PMBHBPh).

Sorption studies using batch method. ***Optimized parameters.*** The effect of pH on both polymeric resins (PMBHBPn & PMBHBPh) was observed by using different buffers with pH 2-10 to obtain maximum % sorption of each metal ions at appropriate pH. The sorption % became high with rising pH of solution and

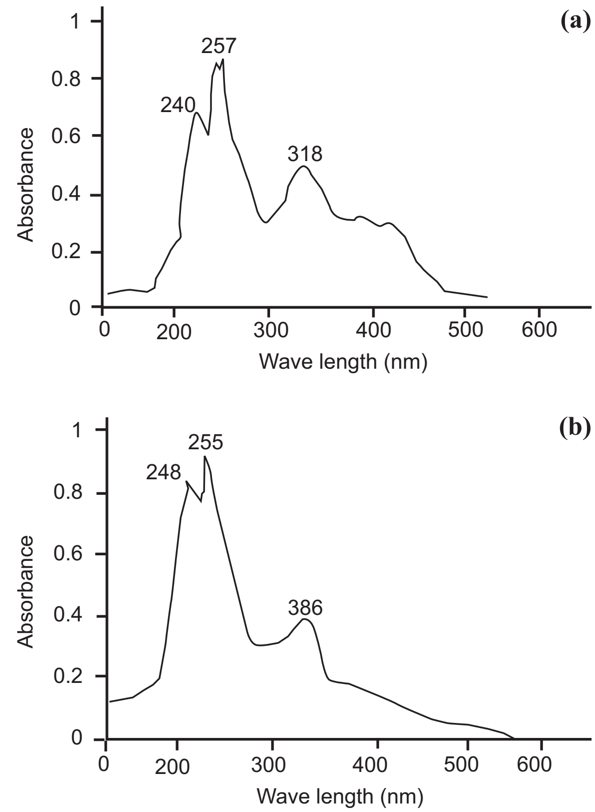


Fig. 3(a-b). UV-visible spectra of (a) (PMBHBPn) (b) (PMBHBPh).

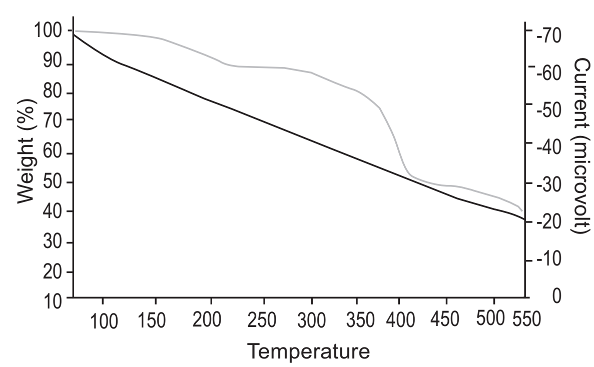
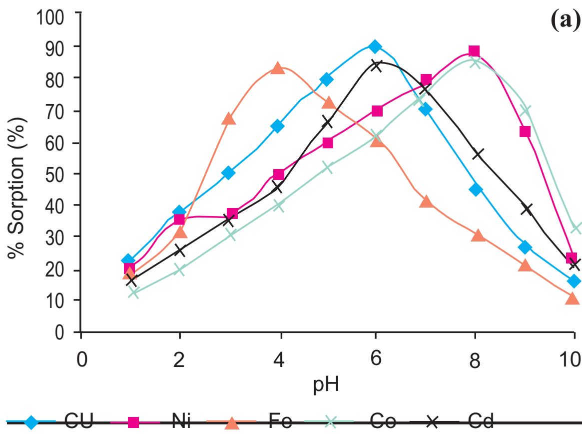


Fig. 4. TG thermograph of Poly[5,5'-methylenebis (2-hydroxybenzaldehyde)1,2-propylenediimine].

attained a maximum value at pH 4 for Fe(III), pH 6.2 for Cu(II) and Cd(II) but pH 8 for Co(II) and Ni(II) metal ions. The metal uptake activities of resins improved the alkalinity of C=N at higher pH with maximum % sorption. The results are shown in Fig. 5(a-b).



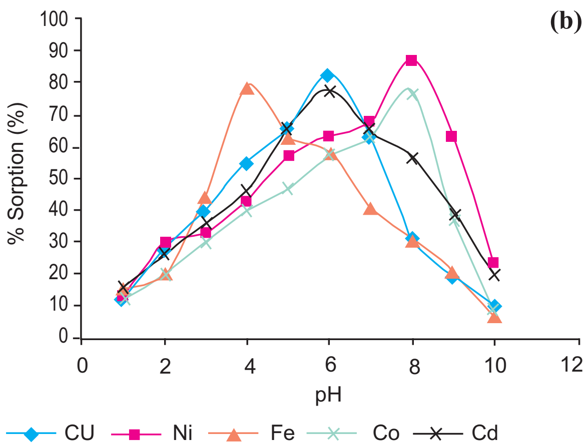


Fig. 5(a-b). Effect of pH on resin (PMBHBPn) for % sorption of Cu(II), Co(II), Ni(II), Fe(III) and Cd(II) using batch method.

Sorption isotherms. The efficiency of Cu(II), Ni(II), Fe(III), Co(II) and Cd(II) metal ions on both polymeric resins was determined by the help of different isothermal equations, which are shown as below:

Freundlich equation:
(log Cads =log A+ (1/n) log Ce. .... (5)

Langmuir equation:
(Ce/Cads) = (1/Qb) + (Ce/Q) .... (6)

Dubinin -Radushkevich equation:
(ln Cads = ln Xm $-\beta\varepsilon^2$) .... (7)

where:

ε = calculated by RT ln (1+(1/Ce)) equation, Ce is the amount of metal ions in the liquid phase at equilibrium and Cads is the amount of metal ions adsorbed/mass of adsorbent. The Freundlich (A) (n), Langmuir (Q) (b) and Dubinin –Radushkevich (Xm) (β) were constants listed in Table 1 which concluded that % sorption decrease at low temperature.

Thermodynamic of sorption. The results of enthalpy of activation energy (ΔH), Gibb's free energy (ΔG) and entropy (ΔS) were obtained from the plot of slope and intercept of enthalpy of activation energy for all above metal ions, and given in Table 2. The parameters enthalpy of activation energy and free energy obtained negative results that indicated exothermic reaction and spontaneous nature of the sorption of metal ions.

Stability of sorbent (Desorption). The stability of polymeric sorbents was examined via several loading of resin as well as its % yield of resin recovery. This polymeric resin was checked about 6 times at optimised conditions, indicated high desorption rate and showed that the resins (PMBHBPn & PMBHBPh) were feasible for sorption.

Table 1. Sorption parameters of Cu(II), Co(II), Ni(II), Fe(III) and Cd(II) ions (5.6×10^{-7} to 4.7×10^{-4}M) on synthesized resin (PMBHBPn) (100 mg) at 30 °C

Metal	Freundlich			Langmuir			D-R		
	A (mmol/g)	1/n	R	Q (mmol/g)	B (l/mol)	R	Xm (mmol/g)	E (Kj/mol)	R
Fe(III)	5.43	0.368	0.996	0.05	2.7×10^2	0.98	0.78	12.8	0.95
Ni(II)	4.683	0.35	0.991	0.04	1.6×10^3	0.99	0.69	12.4	0.97
Co(II)	4.31	0.309	0.979	0.05	3.5×10^3	0.99	0.62	10.3	0.99
Cu(II)	3.9	0.26	0.994	0.07	4.2×10^4	0.97	0.37	9.7	0.99
Cd(II)	2.81	0.23	0.998	0.08	5.4×10^4	0.98	0.31	9.02	0.99

Table 2. Thermodynamic parameters of Cu(II), Co(II), Ni(II), Fe(III) and Cd(II) metal ions on polymeric resin (PMBHBPn) 303 K

Metals	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol)	RSD
Fe(III)	-47.27 ± 0.15	-1.48 ± 0.07	-0.103 ± 0.072	0.996
Ni(II)	-45.21 ± 0.43	-2.14 ± 0.05	-0.114 ± 0.009	0.938
Co(II)	-41.28 ± 0.37	-2.25 ± 0.05	-0.123 ± 0.021	0.991
Cu(II)	-52.14 ± 0.08	-1.6 ± 0.02	-0.113 ± 0.043	0.998
Cd(II)	-36.33 ± 0.31	-4.2 ± 0.03	-0.102 ± 0.001	0.929

Interference study. The sorption of all metal ions may be affected due to the presence of different cations and anions which may form variety of metal complexes. Some cations and anions were helpful to examine their interference for both resins (PMBHPn & PMBHBPh) with metal ions under the optimum conditions.

Analytical performance. For the validity of method, the application work was carried out for both resins (PMBHBPn & PMBHBPh), the concentrations of Cu(II) and Ni(II) metal ions were determined from different water samples. The results indicated that the proposed method is reliable and valid for the sorption of other environmental samples.

Conclusion

Polymeric resin has great capacity to adsorbent and removes different metal ions with different characteristics. This work demonstrated that the synthesized polymer resins (2-hydroxybenzaldehyde with aliphatic and aromatic diamines) can successfully remove various metal ions from their dilute solutions. It was also concluded that the percentage of adsorption is Cd(II) > Co(II) > Fe(III) > Ni(II) > Cu(II). The maximum % sorptions of metal ions were decreased at low temperature. All thermodynamic parameters were indicated spontaneous nature and exothermic reaction. Therefore, the rigidity of polymeric resins (PMBHBPn & PMBHBPh) was positively achieved and had least matrix interference with other common ions.

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