Metal complexation on functionalised polymer supports—An adsorption/complexation phenomenon

K Sivadasan Chettiar & K Sreekumar

aDepartment of Chemistry, Devaswom Board College, Sasthamcottah, Kollam, 690 521, India
bDepartment of Applied Chemistry, Cochin University of Science & Technology, Kochi, 682 022, India

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The present study is aimed at preparing polymer metal complexes of Co(II) and Cu(II) under controlled conditions of concentration, time, temperature and pH. The complexes are derived from DVB crosslinked polystyrene and poly(hydroxyethyl methacrylate) supported thiosemicarbazone-transition metal interaction. Crosslinked polymer ligand beads with definite porosity can adsorb metal ions. The question whether metal complexation is a case of adsorption and coordination, is investigated. Kinetics and thermodynamics of adsorption of metal ions on the polymeric ligand with proper surface structures is determined. The equilibrium metal intake by 10 and 15% crosslinked resins at constant temperature was utilised to construct Langmuir and Freundlich adsorption isotherms. The influence of temperature on the extent of adsorption was studied by plotting isotherms at different temperatures and calculating different thermodynamic parameters.

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Crosslinked polymers properly functionalised to attach ligand moieties are important in preparing macromolecular metal chelates. These materials are economically more advantageous, since they are heterogeneous rather than homogeneous. Among the various applications of these supported metal complex species, their use in pre-concentration and separation of metal ions and heterogeneous catalysis is important. The importance of these materials is clear from the innumerable amount of work carried out in this field and the active work going on in current research. Recently, the study of macromolecular metal complexes has reached the level of supramolecular organization. Polymer supported Schiff base metal chelates are important in the field of selective chelation of metal ions. Schiff base thiosemicarbazone metal complexes of transition metals supported on crosslinked polystyrene (PS), and poly hydroxyethyl methacrylate (PHEMA) serve this purpose. Resins based on polystyrene support, may be showing only low metal ion uptake kinetics. This may be due to the hydrophobic character of the polymer backbone, even though the functional group possess hydrophilic nature. Resins based on hydrophilic polymers like PHEMA, properly crosslinked, have been found to be convenient.

In the study of metal complexation on thiosemicarbazone, supported on divinyl benzene (DVB)-crosslinked PS and PHEMA resins here, metal chelation was achieved on the basis of the development of optimum conditions of time, pH, solvent and crosslink density of the polymer support. The complexation conditions were optimised to have maximum metal ion binding by polymer ligands.

The question whether metal complexation on crosslinked polymer supported Schiff base thiosemicarbazone is a case of complexation as well as adsorption, was examined in detail in the present investigation. Adsorption studies were carried out using 15% DVB-crosslinked polystyrene thiosemicarbazone resins and 10% DVB-PHEMA thiosemicarbazone resins (15% DVB-PST and 10% DVB-PHEMAT).

Experimental Procedure

Styrene, divinylbenzene (DVB) and hydroxyethyl methacrylate (HEMA) were obtained from Fluka. Commercial grade styrene, DVB and HEMA were washed with aqueous NaOH (1-2%) to remove the stabilizers and were then washed with water and dried over anhydrous CaCl₂.
Elemental analyses were done at RSIC, Lucknow. IR spectra were recorded on a Shimadzu model 408 Spectrophotometer using KBr pellets. UV/Vis spectra were recorded on a Shimadzu model 160A double beam Spectrophotometer. ESR spectra were recorded with a Varian 104 Spectrometer. Magnetic measurements were done using Guoy balance. DVB-crosslinked resins of polystyrene and PHEMA of crosslink densities 15 and 10%, respectively were prepared by free radical suspension polymerization. The crosslinked resin, DVB-PS was chloromethylated by adopting standard procedures so as to prepare aldehyde resin.

Preparation of aldehyde resin

Preparation of DVB-PS aldehyde resin

Chloromethylated polystyrene resin (20g), DMSO (300 mL) and NaHCO₃ (19 g) were refluxed at 138-140°C for 14h. The aldehyde resin formed was filtered, washed with hot water and with dioxane-water (1:1 v/v). Finally, the resin was washed with dioxane, ethanol, dichloromethane and benzene (20 mL × 5 times each) and dried under vacuum (yield, 15g).

Preparation of DVB-PHEMA aldehyde resin

DVB-PHEMA resin (15g) was mixed with KMnO₄ (3.2 g) and anhydrous sodium carbonate (2g). The mixture was added after dissolving in water. The contents were refluxed for 5h on a boiling water bath. After removing the excess MnO₂ (by adding sodium sulphite and conc. HCl), the aldehyde polymer was filtered, washed with water (20 mL × 5 times), acetone (10 mL × 3 times) and then dried (yield, 12g).

Conversion of aldehyde polymer to Schiff base polymer

The aldehyde polymer (10g) was swollen in alcohol (50mL), and was mixed with thiosemicarbazide (15g). The mixture was refluxed (10h). The Schiff base resin was washed with alcohol, water and acetone (10mL × 5 times). The resin was dried at 50°C and kept under vacuum desiccation.

Metal chelation-adsorption experiments

The adsorption experiments involved the formation of Schiff base polymer metal complexes, by equilibrating the polymer ligand with an aqueous solution of suitable metal ion. Experiments were done with metal ions Cu(II) and Co(II) of different initial concentrations using the resins, 10 and 15%, DVB-PHEMAT and DVB-PST.

Varying concentrations of metal ions (20mL, 4 × 10⁻³ to 2 × 10⁻² M) of Cu(II) and Co(II) were taken in numbered stoppered bottles containing 1g each of the polymer ligand. The solution was stirred for 10h, so that equilibrium of metal ion with the resin was attained (as observed by analysis – aliquots of clear supernatant liquid was withdrawn and analysed for determining the equilibrium metal ion concentration, thereby calculating the metal ions absorbed by 1g of the resin).

Results and Discussion

Aldehyde polymer, corresponding to different resins was prepared. 15% DVB-PS chloromethylated resin was converted to aldehyde resin by oxidation with dimethyl sulphoxide (DMSO) in presence of NaHCO₃. Oxidation of 10% DVB PHEMA resin in basic medium was done by dil. KMnO₄ in the presence of anhydrous sodium carbonate. The aldehyde polymer obtained in each case was condensed with thiosemicarbazide to form polymer supported thiosemicarbazone resins i.e., 15% DVB-PST and 10% DVB-PHEMAT. These polymer ligands were equilibrated with metal ions Cu(II) and Co(II) to form the metal chelates. They showed comparatively higher metal intake capacity than expected. The higher metal intake may be explained by considering metal complexation as an adsorption/complexation phenomenon.

The metal complexes were characterized by elemental analysis, spectral study and magnetic moment measurements with a view to have a geometry assigned. The spectral study involved IR, UV/Vis and ESR measurements.

Rate study and equilibrium

Batch experiments were carried out by shaking known volumes of copper ion and cobalt ion solutions of definite concentration with definite amount of DVB-PST and DVB-PHEMAT resins in separate experiments. Aliquot amounts of solutions were withdrawn at definite time intervals from the supernatant liquid, and the amounts of Co(II) and Cu(II) remaining at equilibrium were determined. The equilibrium concentration values were used to calculate the amount of metal ion adsorbed by 1 g of the resin, knowing the initial metal ion concentrations. The rate at which equilibrium is attained depends on the nature of metal ion involved in the resin reaction. This is observed in the adsorption time course for Cu²⁺ ion and
Co$^{2+}$ ion at 30 and 50°C on 15% DVB-PST resin (Fig. 1). The DVB-PST resin forms a more stable state at equilibrium with Cu$^{2+}$ ion than Co$^{2+}$ ion. This depends on the rate of adsorption.

**Adsorption/complexation mechanism**

The adsorption time course curve (Fig. 1), shows a double nature—curved and linear. The curved portion represents film diffusion followed by intraparticle diffusion as shown by linear portion. The pore diffusion coefficient depends on the initial metal ion concentration and shaking speed. Here, since the initial metal ion concentration in solution is low, the diffusion of metal ions in the boundary layer is reduced. Moreover, the shaking speed is greater. All these factors enhance intraparticle diffusion.

The metal ion adsorption process of a chelating resin, involves diffusion of metal ion from the bulk of the solution to the outer surface (mass transfer). This is followed by internal diffusion into the pores. 10% and 15% DVB-PST resins, properly functionalised, having developed surface, and surface porosity can act as effective adsorbents in metal ion complexation.

**Surface parameters of the adsorbent**

The porosity of the resins used as adsorbent, is estimated quantitatively by several parameters like specific surface area, $S_{sp}$, total pore volume $W_0$ and pore radius, $r$. The surface parameters for DVB-PST and DVB-PHEMAT resins are given in Table 1.

The pore diffusion coefficient $D$ for adsorption of Cu(II) and Co(II) on DVB-PST resin depends on the initial concentration of the metal ion, shaking speed and temperature. The $D$ value can be calculated by using the equation,$^{12}$

$$D = \frac{0.03r_0^2}{t_{1/2}},$$

where $r_0$ is the particle radius. The time for half adsorption is given by $t_{1/2}$. The pore diffusion coefficient, calculated for the adsorption of Cu(II) and Co(II) on 15% DVB-PST resin is given in Table 2.

**Adsorption by DVB-PST**

The equilibrium uptake of metal ions by the 15% DVB-PST resin occurred within a period of 360 to 400 min. The experimental observations were processed to fit in Langmuir and Freundlich isotherms. The quantity of metal ion adsorbed per unit mass of the adsorbent ($x/m$) at varying initial concentrations ($C_0$) of metal ions was calculated from the concentration remaining at equilibrium ($C_e$).

Langmuir adsorption plots of $\ln x/m/C_e$ against $x/m$ for Cu$^{3+}$ and Co$^{2+}$ ions adsorption at 30 and 50°C are given in Figs 2 and 3. The plots are found to be linear, which indicates the applicability of the Langmuir mode of adsorption. The values of the reaction quotients at 30 and 50°C are calculated from these plots by applying limit,$^{11}$

$$\lim_{x/m \to 0} \frac{\ln x/m}{C_e} = K_o,$$

the reaction quotient. Thus extrapolating to zero concentration, i.e. $x/m$, of the value of plot of $\ln x/m/C_e$ versus $x/m$, will give the thermodynamic equilibrium constants (reaction quotient). Knowing the thermodynamic equilibrium constants at two different temperatures, the standard en-
enthalpy change ($\Delta H^\circ$) was calculated using van’t Hoff isochore,

$$\ln \frac{K_{OT1}}{K_{OT2}} = -\frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

Other thermodynamic parameters like, standard free energy change ($\Delta G^\circ$) and standard entropy change ($\Delta S^\circ$), were also determined using equations $\Delta G^\circ = -RT\ln K^\circ$ and $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. The thermodynamic parameters, thus, calculated for the adsorption of Co$^{2+}$ and Cu$^{2+}$ on 15% DVB-PST at different temperatures, i.e., 30 and 50°C are given in Table 3.

The free energy change shows a decrease at higher temperature, showing the increase in feasibility of adsorption. The standard enthalpy change, shows a positive value showing an endothermic nature of adsorption. The standard free energy change shows a decrease for Co(II) and Cu(II) adsorption. In the case of Co$^{2+}$ adsorption, the standard free energy change shows only smaller decrease. Thus, adsorption is feasible at higher temperature for Cu(II) and Co(II). The standard entropy change ($\Delta S^\circ$) shows a positive value, suggesting an increase in randomness. The above facts show, that, the thermodynamic parameters of adsorption of Cu$^{2+}$ and Co$^{2+}$ ions by DVB-PST ligand is in agreement with the increase in adsorption observed at higher temperature$^{13}$.

### Table 3 – Adsorption of Cu(II) and Co(II) on 15% DVB-PST

<table>
<thead>
<tr>
<th>Adsorbate (metal ion)</th>
<th>Temperature (K)</th>
<th>Reaction quotient ($K_\circ$)</th>
<th>Thermodynamic parameters</th>
<th>Std. free energy $\Delta G^\circ$ (KJ/mole)</th>
<th>Std. enthalpy change $\Delta H^\circ$ (KJ/mole)</th>
<th>Std. entropy change $\Delta S^\circ$ (KJ/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^{2+}$</td>
<td>303</td>
<td>0.10</td>
<td></td>
<td>5.80</td>
<td>158.38</td>
<td>0.50</td>
</tr>
<tr>
<td></td>
<td>232</td>
<td>4.90</td>
<td></td>
<td>-4.27</td>
<td>4.78</td>
<td></td>
</tr>
<tr>
<td></td>
<td>303</td>
<td>0.15</td>
<td></td>
<td>4.78</td>
<td>4.78</td>
<td></td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>323</td>
<td>1.40</td>
<td></td>
<td>-0.90</td>
<td>90.93</td>
<td>0.28</td>
</tr>
</tbody>
</table>

$^a$Natural pH; Time of stirring, 6h; Aqueous solution

Adsorption parameters: Sorption energy and sorption capacity

The adsorption parameters such as sorption energy ($b$) and sorption capacity ($Q^\circ$) are obtained from the isotherm plots based on modified Langmuir equation,

$$\frac{C_e}{x/m} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ},$$

where ‘$b$’ is the sorption energy and $Q^\circ$ is the sorption capacity.

The plots of $C_e/x/m$ against $C_e$ is found to be a straight line for Co$^{2+}$ and Cu$^{2+}$ ion adsorption on 15%
CHETTIAR & SREEKUMAR: METAL COMPLEXATION ON FUNCTIONALISED POLYMER SUPPORTS

63

Fig. 4—Adsorption of Cu(II) on 15% DVB-PST. Langmuir adsorption isotherm at (a) 30 and (b) 50°C

Fig. 5—Adsorption of Co(II) on 15% DVB-PST. Langmuir adsorption isotherm at (a) 30 and (b) 50°C

DVB-PST at different temperatures (Figs 4 and 5). From the slope of the graph, $Q^o$ is calculated, and knowing the intercept, $1/Q^o b$, the sorption energy $'b'$, is determined. The calculated values of sorption energy and sorption capacity are given in Table 4, for adsorption of Co$^{2+}$ ion and Cu$^{2+}$ ion. The high values of sorption energy, clearly shows that adsorption is feasible at higher temperature. Thus, higher temperature may favour higher diffusion to the surface of adsorbent.

Freundlich adsorption plots are also in agreement with the observations made above. The logarithmic form of the equation is,

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C_e$$

The plot of $\log \frac{x}{m}$ against $\log C_e$ is found to be a straight line (Figs 6 and 7). $k$ and $1/n$ are Freundlich constants for the given system and temperature.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Metal ion</th>
<th>Sorption capacity $Q^o$ (mg/g)</th>
<th>Sorption energy $b^o$ (L/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>Cu(II)</td>
<td>0.02</td>
<td>16.66</td>
</tr>
<tr>
<td>323</td>
<td>Cu(II)</td>
<td>0.013</td>
<td>78.12</td>
</tr>
<tr>
<td>303</td>
<td>Co(II)</td>
<td>0.032</td>
<td>39.55</td>
</tr>
<tr>
<td>323</td>
<td>Co(II)</td>
<td>0.007</td>
<td>266.66</td>
</tr>
</tbody>
</table>

Freundlich constants and correlation coefficients for the adsorption of Co(II) and Cu(II) on 15% DVB-PST are given in Table 5.

$\gamma$ is the correlation coefficient. The nearer value of $'\gamma'$ to +1 shows, that there is a greater probability, that a definite linear relationship exists between $\log C_e$ and $\log \frac{x}{m}$. The value of the Freundlich constant $1/n$ is found to be less than ‘1’ for adsorption of
Fig. 8—Adsorption of Co(II) on 10% DVB-PHEMAT. Langmuir adsorption isotherm at (a) 30 and (b) 50°C shows a straight line in agreement with Langmuir plot (Fig. 8). Thermodynamic parameters are calculated from the plot of $\ln{x/m/C_e}$ versus $C_e$ (Fig. 9). The values of sorption capacity and sorption energy (calculated from the slope and intercept of the plots) together with thermodynamic parameters for adsorption of Co(II) are given in Table 6.

Eventhough sorption energy shows an increase at higher temperature, as is expected, the sorption capacity of the resin shows a lower value. There may thus be a chance of desorption of the adsorbed species at higher temperature and higher shaking speed.

The negative value of $\Delta H^o$ shows that the adsorption process is exothermic in nature. This is in agree-

### Table 5 – Freundlich constants for the adsorption of Co(II) and Cu(II) on 15% DVB-PST

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Metal ion</th>
<th>Freundlich constants</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$1/n$</td>
<td>$k$</td>
</tr>
<tr>
<td>303</td>
<td>Cu(II)</td>
<td>0.09</td>
<td>1.73 x 10^{-2}</td>
</tr>
<tr>
<td>323</td>
<td>Cu(II)</td>
<td>0.83</td>
<td>4.08 x 10^{-2}</td>
</tr>
<tr>
<td>303</td>
<td>Co(II)</td>
<td>0.58</td>
<td>8.12 x 10^{-3}</td>
</tr>
<tr>
<td>323</td>
<td>Co(II)</td>
<td>0.86</td>
<td>1.73 x 10^{-2}</td>
</tr>
</tbody>
</table>

### Table 6 – Langmuir constants and thermodynamic parameters for the adsorption of Co(II) on 10% DVB-PHEMAT

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Langmuir constants</th>
<th>Thermodynamic parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sorption capacity</td>
<td>Sorption energy</td>
</tr>
<tr>
<td></td>
<td>$Q^o$ (mg/g)</td>
<td>$b^o$ (L/g)</td>
</tr>
<tr>
<td>303</td>
<td>0.10</td>
<td>19.23</td>
</tr>
<tr>
<td>323</td>
<td>0.04</td>
<td>30.52</td>
</tr>
</tbody>
</table>

**Adsorption by DVB-PHEMAT**

DVB-PHEMAT resins also obey adsorption isotherms. But the hydrophilicity of the resin causes some variation from DVB-PST resin.

The adsorption of Co(II) and Cu(II) on 10% DVB-PHEMAT also follows Langmuir and Freundlich adsorption isotherms. In the case of Co(II) adsorption on 10% DVB-PHEMAT, the plots of $C_e/x/m$ against $C_e$ shows a straight line in agreement with Langmuir plot (Fig. 8). Thermodynamic parameters are calculated from the plot of $\ln{x/m/C_e}$ versus $C_e$ (Fig. 9). The values of sorption capacity and sorption energy (calculated from the slope and intercept of the plots) together with thermodynamic parameters for adsorption of Co(II) are given in Table 6.

Eventhough sorption energy shows an increase at higher temperature, as is expected, the sorption capacity of the resin shows a lower value. There may thus be a chance of desorption of the adsorbed species at higher temperature and higher shaking speed.

The negative value of $\Delta H^o$ shows that the adsorption process is exothermic in nature. This is in agree-

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Fig. 9—Adsorption of Co(II) on 10% DVB-PHEMAT. Langmuir adsorption isotherm at (a) 30 and (b) 50°C
ment with the positive value of $\Delta G^\circ$ showing that there is increase in surface energy of the system, which is not lowered. The above facts are supported by the negative value of entropy change, $\Delta S^\circ$. The process of randomness at the solid-solution interface is not observed. Thus, adsorption of Co(II) on 10% DVB-PHEMAT is not feasible at higher temperature. This may be due to the hydrophilic nature of the polymer support, unlike, the hydrophobic nature observed for DVB-PST.

The Freundlich adsorption isotherm plots (Fig. 10) also support the above facts. The plots are found to be linear and are in agreement with high ‘$\gamma$’ values. The values of Freundlich constant (1/$n$) are greater than 1 especially at higher temperature (Table 7).

The Freundlich constant $k$ shows a very low value. This is also in agreement with earlier findings, based on Langmuir isotherm, especially at higher temperature.

In the case of adsorption of Cu(II) on 10% DVB-PHEMAT at 30 and 50°C, the Langmuir constants and thermodynamic parameters calculated from Langmuir adsorption plots (Figs 11 and 12), are in agreement with a positive adsorption. The Langmuir constants and thermodynamic parameters calculated, are given in Table 8.

The value of sorption energy shows an increase at higher temperature. The thermodynamic parameters calculated from the plot of $\ln x/m/C_e$ versus $x/m$ shows that adsorption is favourable in the case of Cu(II) on 10% DVB-PHEMAT. The standard enthalpy change

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Freundlich constants</th>
<th>Correlation coefficient, $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>$3.02 \times 10^{-2}$</td>
<td>1.08</td>
</tr>
<tr>
<td>323</td>
<td>$2.82 \times 10^{-2}$</td>
<td>1.35</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Sorption capacity $Q^\circ$ (mg/g)</th>
<th>Sorption energy $b$ (L/g)</th>
<th>Reaction quotient $K^\circ$</th>
<th>Standard enthalpy change $\Delta H^\circ$ (KJ/mole)</th>
<th>Standard free energy change $\Delta G^\circ$ (KJ/mole)</th>
<th>Standard entropy change $\Delta S^\circ$ (KJ/mole)</th>
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</thead>
<tbody>
<tr>
<td>303</td>
<td>0.014</td>
<td>187.96</td>
<td>0.76</td>
<td>8.16</td>
<td>-1.12</td>
<td>0.025</td>
</tr>
<tr>
<td>323</td>
<td>0.008</td>
<td>367.64</td>
<td>1.52</td>
<td></td>
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</tbody>
</table>
Fig. 13—Adsorption of Cu on 10% DVB-PHEMAT. Freundlich adsorption isotherm at (a) 30 and (b) 50°C

Table 9—Freundlich constants and correlation coefficient ($\gamma$), for adsorption of Cu(II) on 10% DVB-PHEMAT ligand

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Freundlich constants</th>
<th>Correlation coefficient, $\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>303</td>
<td>$2.40 \times 10^{-2}$</td>
<td>0.73</td>
</tr>
<tr>
<td>323</td>
<td>$1.2 \times 10^{-2}$</td>
<td>0.42</td>
</tr>
</tbody>
</table>

($\Delta H^o$) shows a positive value. Thus, increase in temperature is favourable.

The observations are in agreement with high standard entropy change ($\Delta S^o$) and a decrease in free energy change ($\Delta G^o$). The influence of agitation and higher temperature in enhancing the rate of intraparticle diffusion is thus supported for adsorption of Cu(II) on 10% DVB-PHEMAT. The Freundlich isotherm plots of Cu(II) (Fig. 13) also explain the observed phenomena. The values of $1/n$ are found to be less than 1 (Table 9), showing that the adsorption of Cu(II) on 10% DVB-PHEMAT is favourable at higher temperature, in agreement with Langmuir findings. The correlation coefficients observed clearly relate the plot to log$x/m$ versus log$C_e$.

**Conclusion**

DVB-PST and DVB-PHEMAT polymeric ligands of higher crosslink density, usually 10 and 15%, showed comparatively higher metal intake than expected. The higher metal intake may be explained by considering metal complexation as an adsorption phenomenon. 10 and 15% crosslinked resins have developed surfaces in addition to porous nature, which enhances diffusion through the channels and pores. Thus, network structure of the polymer is expected to provide additional metal intake ability, by secondary forces of dispersion and residual valence forces. The change in adsorption phenomenon as a result of change of support from hydrophobic to hydrophilic matrix is evaluated. The adsorption data are useful in preconcentration and separation of metal ions like Cu(II) and Co(II) from field samples. The polymer support provides a heterogeneous base for separation/treatment of effluents.

**References**