

**Research Article**

# SEPARATION OF SOME HEAVY METAL SPECIES FROM ELECTROPLATING RINSING SOLUTIONS BY ION EXCHANGE RESIN

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## Abstract

Strongly basic anion exchange lewatis MP 600 resin was tested to separate metal species from electroplating rinsing wastewater. An azo resorcinol 4-(2-pyridylazo) dyestuff was used as a complexing agent. Adsorption isotherms have been modeled in ethanol/acetic acid/water media. The loaded resin is regenerated using 4 M HCl whereby the eluted metal species are recovered. Results revealed that mere anion exchanger cannot uptake metal ions unless they reacted with the dye to form negatively charged complexes. Trivalent chromium showed significant uptake at pH range of 3.5-4.5. Cadmium, zinc and nickel ions formed complex compounds in the alkaline medium. The electrostatic interaction and formation of complex compounds identified the major adsorption mechanisms. The uptake capacity of the sorbent is directly proportional to the electro negativity of the metal-dye complexes. Ethanol and acetic acid enhanced formation of the dye-metal complexes by decreasing the dielectric constant of the ethanol/acetic acid-water ternary system. **Copyright © acascipub.com, all rights reserved.**

**Keywords:** ion exchange, separation and purification, waste and pollution control.

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## 1. INTRODUCTION

Wastewater generated in rinsing electroplating processes is loaded with substantial amounts of heavy metal species. Among the developed technologies (e.g., ion exchange, filtration, coagulation and adsorption), however, adsorption has been shown to be the most effective one [1] Polymers are industrially attractive because they are capable of binding transition metal ions, widely available and environmentally safe. The main advantage of ion exchange method is that it promotes recovery of the metal species and regeneration of the resin, selectivity and less sludge formation [2]. Hu et al. 2008 [3], studied the removal of vanadium from molybdate solution by ion exchange technique using strong basic resin D296 at a pH value 7.2. Vanadium concentration was 0.6 g/L while molybdenum concentration was 60-80 g/L and the chloride ions 20 g/L. It was reported that vanadium separation could only be performed in the pH range of 6.5-8.5. Chloride ions had important influence so that it was

impossible to remove vanadium when the chloride concentration increased near 70 g/L. Hamadi et al. [4] showed that maximum adsorption of chromium ions being observed at pH range 3.5 – 4 for Lewatit MP 600 resin.

Molinaa et al. [5] studied the nature of complexes produced in the reaction between Zn(II) and Cd(II) and 4-(2-pyridylazo) resorcinol resin sorbed on Sephadex QAE anion exchanger. The stoichiometry of the complexes was 1:2 metal species: ligand. A retention model for the chelates of Ni(II), Fe(II) and Cu(II) whereas Co(II) chelate exhibited anomalous behavior had been reported by Pavil [6]. The chelate retention was strongly affected by the presence of methanol in the mobile phase. Kravchenko et al. [7], **studied** the chemical precipitation of copper from copper-zinc solutions onto weakly basic anion exchangers in their free base forms. The process was investigated in both, batch and packed bed experiments. The authors reported that copper was recovered at pH range 6-8. Smolik et al [8], studied the sorption behavior and possible separation of zirconium and hafnium from acid solution using Diphonix chelating resin. The best possible separation of these elements was obtained in 0.5 M H<sub>2</sub>SO<sub>4</sub> at 22°C. The uptake of copper, nickel, cobalt, lead, iron and manganese from manganese chloride leach solution onto the chelating resin Dowex M-1495 was studied (Claudia et. [9]). Results demonstrated the ability to remove contaminants to an extent satisfying the quality criteria required for the utilization of manganese chloride solution for preparing manganese chemicals.

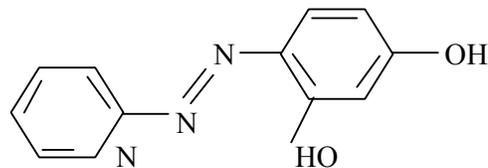
Edel et al. [10] studied the effect of flow conditions up to 5 mL/min for the separation of Cu<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup> and Mn<sup>2+</sup> in column reaction with dyestuff 4-(2- pyridylazo) resorcinol. The authors showed that total runs times could be reduced to fewer 4 minutes. Abdel-Aal [11] studied the distribution coefficient K<sub>d</sub> for the resorcinol separation of Co(II), Pb(II), Cr(III) and Al(III) between Amberlite IRA-401 ion exchanger in presence of C.I. Mordant Black 9 resin-organic solvent– nitric acid media. The K<sub>d</sub> value was markedly higher in acetone-resin water nitrate media than those given in aqueous–methanol-resin-nitrate. Yuezhou et al [12] studied the use of Amberlite IRA-900 and a novel silica-based anion exchanger AR-01 in the same media. They reported complete separation of Co(II) from Ni(II) and Cu(II) from Ni(II) in column experiments. Compared to IRA-900, AR-01 showed faster adsorption and elution kinetics. Syed et al [13] modified Amberlite IR-400 with naphthol blue-black. Some important binary separation of metal ions of analytical interest was exploited. Inglezakis and Loizidou [14] studied the use of polar organic solvents (pure ethanol and acetone) for possibility of ion exchange technique and natural zeolite clinoptilolite to separate heavy metal ions. They concluded that ion exchange of metal species using zeolite was possible to take place in polar organic solvents but selectivity could be totally changed. The aim of this work is to separate Cr<sup>3+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup> and Ni<sup>2+</sup> ions from rinsing wastewater of electroplating industry using a strong basic anion exchange resin Lewatit MP 600 macro porous type-II. A resorcinol azo dyestuff 4-(2- pyridylazo) was used to form complex compound with the metal species. Parameters affecting the sorption extent such as the resin mass, metal ions concentration, pH, the dyestuff dosage and ethanol and acetone concentration were investigated.

## 2. Experimental

### 2.1 Materials

2.1.1 The anion exchange resin Lewatit MP 600 (Merk) was converted to a chloride form by running 2 M HCl acid for 3 days. The resin was then washed with aqueous ethanol (70%) and dried under vacuum at 25°C.

2.1.2 The dye solution: A stock solution 0.01M of the dyestuff: 4-(2- pyridylazo) resorcinol (Merk) having a molecular weight 215.21 was prepared by dissolving 0.538g in 0.25 L 80 % aqueous ethanol. Fig 1 shows the structure of the dye.



**Figure 1:** The structure of the resorcinol dye.

2.1.3 Buffer solutions used were a mixture of 0.2M bi-sodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$ , and 0.1 M citric acid  $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$  for pH control.

2.1.4 Acetic acid solutions of 0.1M – 1M were prepared by dilution of glacial acetic acid with bi-distilled water. Aqueous ethanol solutions were prepared by diluting anhydrous alcohol with de-ionized water by volume. Similarly, aqueous acetone solutions were prepared from analytical grade acetone.

2.1.5 The synthetic solution of metal species

Dilute synthetic salt solutions up to 1000 ppm of  $\text{CrCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2$  and  $\text{NiCl}_2$  were prepared from pure chemicals. A similar set of experiments were carried out using the industrial rinsing waste solution.

2.1.6 Hydrochloric acid 4 M was used as an eluent solution.

## 2.2 Description of the method

About 200 mg of the chloride-resin was placed in a glass column 9 mm inner diameter with a glass wool support at its end. The synthetic metal(s) solutions were poured to pass over the resin at a flow rate of 0.2 mL/min. An aliquot samples were taken throughout the running test for analysis. At the end of each experiment, the resin was rinsed with de-mineralized water to flush unabsorbed metal species away. Metal ions accumulate on the resin until equilibrium conditions are attained, i.e. free ion bound to the resin is constant. For solutions containing no ligand, equilibrium is considered to be reached when the concentration of free ion in the effluent (leaving the column) corresponds to that in the sample solution ( $[\text{M}^{2+}]_{\text{eff}} = [\text{M}^{2+}]_{\text{sol}}$ ) (Cantwell [15]). The bound metal species were eluted using 4 M HCl acid flowing at a rate of 0.5 mL per minute. The effluent was collected in 10 mL fractions for analysis with the help of absorption spectrophotometer. In a similar set of experiments, the dye was added to the metal ions solutions before running the adsorption process. The same dye dosage was used to both the synthetic and industrial waste solutions. The pH value of the metal solutions was controlled by addition of buffering agents.

## 2.3 Methods of measurements

2.3.1 Determination of chromium, zinc, cadmium and nickel ions was carried out with the help of a UV-visible atomic absorption spectrophotometer Milton Roy model 20D for the resin and the metal species ions determination.

2.3.2 Determination of the pH value was carried out with a based bench pH meter (Hanna model 211) fitted with HF1131B electrode. Measurements were conducted at  $25^\circ\text{C} \pm 0.2^\circ\text{C}$ .

2.3.3 The capacity of the resin to bound metal species  $\epsilon_r$  was calculated by the equation given by Fenge Li et al. [16] 2005:

$$\epsilon_r = \frac{(M_o^{2+} - M_e^{2+}) V}{m_{\text{res}}} \quad (\text{g metal / g resin}) \dots\dots\dots (1)$$

$M_o^{2+}$  and  $M_e^{2+}$  represented initial and equilibrium concentration of the metal species respectively, which was measured by the atomic absorption spectrophotometer, V was the volume of solution and  $m_{\text{res}}$  was the mass of the resin.

2.3.3 The concentration of metal species bound to the resin ( $\text{mol g}^{-1}$ ), {M-R} was determined experimentally by eluting a known mass of loaded resin ( $m_{\text{res}}$ ) with a known volume of the eluate  $V_{\text{el}}$  (L).

$$\{\text{M-R}\} = \frac{[\text{M}^{2+}]_{\text{el}} \times V_{\text{el}}}{m_{\text{res}}} \quad \text{g metal / g resin} \dots\dots\dots (2)$$

where  $[\text{M}^{2+}]_{\text{el}}$  is the concentration of metal in the eluate ( $\text{mol L}^{-1}$ ).

2.3.4 The partition coefficient  $K_d$  ( $\text{Lg}^{-1}$ ) represents the ratio of concentration of free ions for one metal species bound to the solid phase here the resin exchanger {M-R} and in the liquid phase. It was determined by calibrating with solutions of known  $[\text{M}^{2+}]$ , having identical ionic compositions and conditions of pH and T as found in the analyte solutions (Worms and Wikenson, [17]).

$$K_d = \frac{\{\text{M-R}\}}{[\text{M}^{2+}]} \dots\dots\dots (3)$$

2.3.4 Sorption extent (%) was determined from the relation reported by Fethiya and Erol [2].

$$\text{Sorption \%} = \frac{(M_o^{2+} - M_e^{2+})}{M_o^{2+}} \times 100 \dots\dots\dots (4)$$

### 3. Results

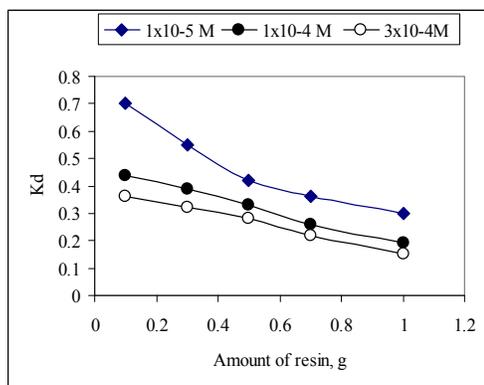
The anion exchange resin used in this study is a strongly basic macro porous (type-II) cross linked polystyrene. Table 1 shows the properties of the resin. The dyestuff is 4-(2- pyridylazo) resorcinol has a chemical formula  $C_{11}H_9N_3O_2$  with molecular weight 215.21.

**Table 1:** The properties of the resin

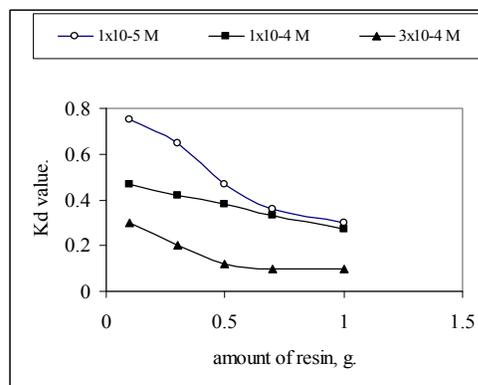
Property	Value
Application	Conventional water treatment
Matrix type	Cross linked polystyrene
Functional groups	Quaternary ammonium (type II).
Standard ionic form	Chloride ion
Resorcinol particle size	0.3 – 1.2 mm
Moisture content	47 – 54
Max. operating temperature	40 °C
Total exchange capacity m. eel/mL	1.1
Volume change, %	OH <sup>-</sup> to Cl <sup>-</sup> (-7 to -17)

#### 3.1 Effect of metal species and concentration on $K_d$ and S%

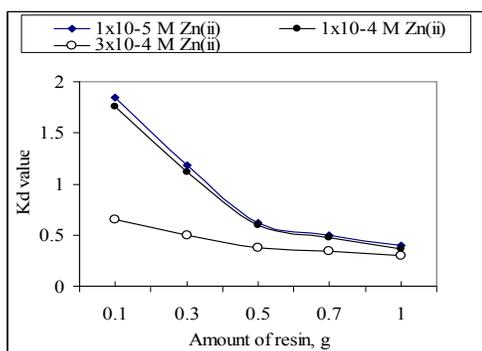
Figures 2a through 2f show the effect of resin amount on the  $K_d$  value and sorption % using  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$  and  $3 \times 10^{-4}$  mole synthetic solutions of  $CrCl_3$ ,  $ZnCl_2$ ,  $Cd(NO_3)_2$  and  $NiCl_2$  (pH=4.5 and T=25°C). It can be seen that  $K_d$  values are nearly negligible and decrease with the increase in both the amount of the resin and metal ion concentration. The sorption percentage is presumably directly proportional to the amount of the res



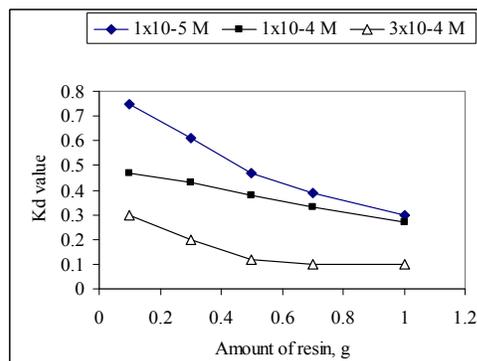
**Figure 2a:**  $K_d$  for synthetic  $Cr^{3+}$  solution.



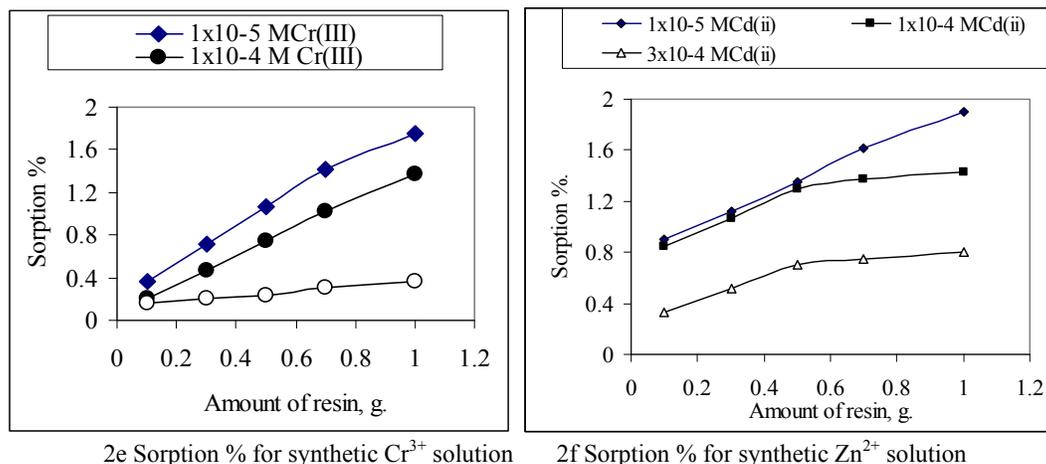
**Figure 2b:**  $K_d$  for synthetic  $Zn^{2+}$  solution.



**Figure 2c:**  $K_d$  for synthetic  $Cd^{2+}$  solution

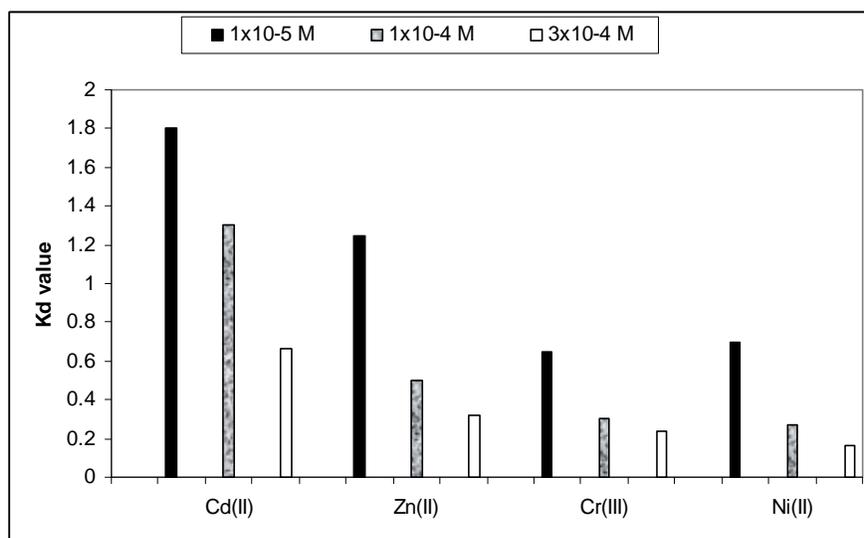


**Figure 2d:**  $K_d$  for synthetic  $Ni^{2+}$  solution

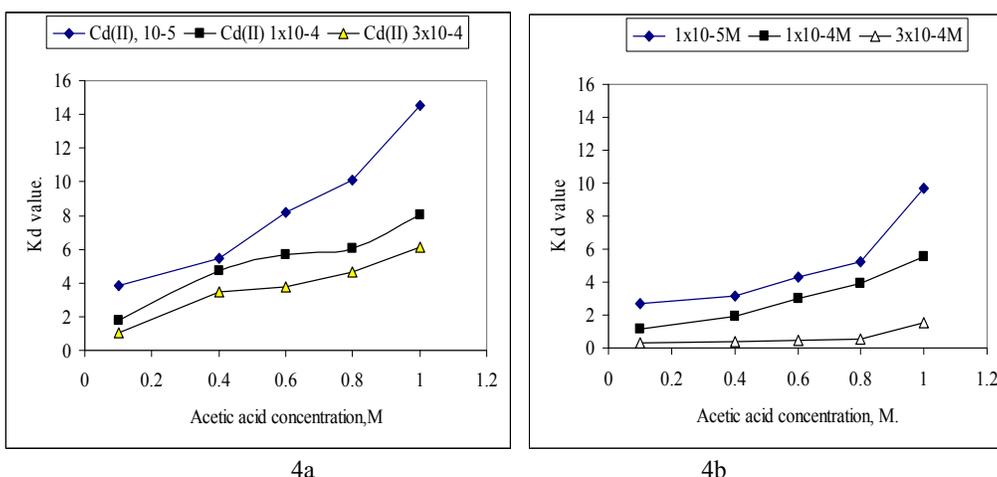


**Figure 2:** Effect of the resin amount on  $K_d$  value and sorption percentage using  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$  and  $3 \times 10^{-4}$  mole synthetic solutions (pH=4.5 and T=25 °C).

Figure 3 shows that the  $K_d$  value is highest with cadmium ions compared to zinc, Cr and nickel ions. The change in  $K_d$  value is significant with dilute solutions ( $1 \times 10^{-5}$  M) as compared to more concentrate ones ( $\geq 10^{-4}$  M). 3.2 Effect of acetic acid addition on  $K_d$  value Figure 4 shows the effect of addition of acetic acid on the  $K_d$  value of synthetic divalent cadmium (4a) and trivalent chromium (4b) solutions having different molarities (T=25 °C). It is seen that addition of acetic acid to the metal solution promotes relative increasing the  $K_d$  value. Acetic acid effect is more seen with dilute metal solutions. For one and the same concentration, the  $K_d$  value obtained with cadmium is comparatively higher than that acquired with chromium solutions.



**Figure 3:** The  $K_d$  value with different metal species ( $\text{CrCl}_3$ ,  $\text{ZnCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2$  and  $\text{NiCl}_2$ ) having different concentrations;  $1 \times 10^{-5}$  M,  $1 \times 10^{-4}$  M and  $3 \times 10^{-4}$  M using 0.1 g resin, at pH 4.5 and T=25°C



**Figure 4:** Effect of acetic acid concentration on K<sub>d</sub> value of synthetic divalent cadmium (4a) and trivalent chromium (4b) solutions having different molarities (T=25 °C).

Figure 5 shows the effect of adding acetic acid to the industrial electroplating rinsing solutions having 1x10<sup>-4</sup> mol (5a) and 3x10<sup>-4</sup> mol (5b) on K<sub>d</sub> value. Experiments were carried out at pH 3.5 at T= 25°C. It is seen that acetic acid addition displays the same effect as with the synthetic solutions i.e. increasing the K<sub>d</sub> value. The K<sub>d</sub> value using dilute rinsing solution of 1x10<sup>-5</sup> mol/L shows the same trend but with higher magnitude. It is also seen that the extent of K<sub>d</sub> is proportional to the acetic acid concentration. The K<sub>d</sub> value decreases in the order Cd(II), Zn(II), Cr<sup>3+</sup> and Ni(II) ions.

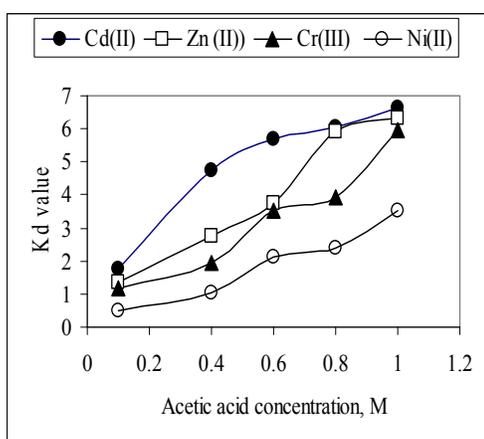


Figure 5a

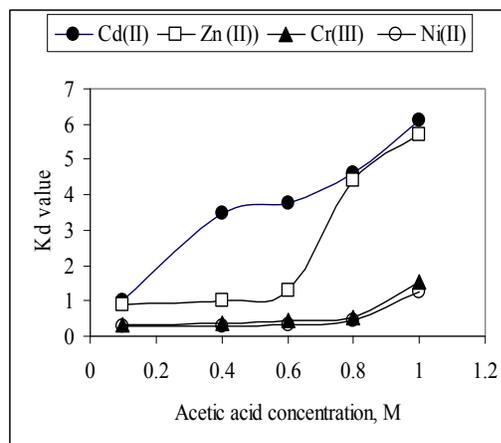
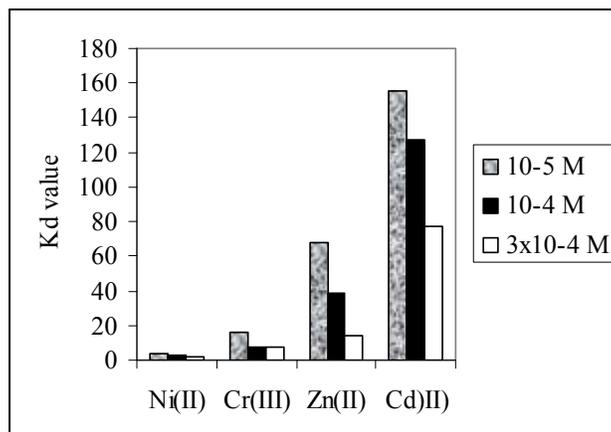


Figure 5b

**Figure 5:** Effect of acetic acid concentration on K<sub>d</sub> value for rinsing solutions having 1x10<sup>-4</sup> mol (5a) and 3x10<sup>-4</sup> mol (5b) at pH= 4.5 and T=25 °C.

### 3.3 Effect of ethanol addition on K<sub>d</sub> value

Figure 6 shows the effect of addition of aqueous ethanol (80% by volume) to the rinsing wastewater on the K<sub>d</sub> value using solutions with different molar concentrations of 1x10<sup>-5</sup> M, 1x10<sup>-4</sup> and 3x10<sup>-4</sup> M for Ni<sup>2+</sup>, Cr<sup>3+</sup>, Zn<sup>2+</sup> and Cd<sup>2+</sup> without acetic acid at 25°C. It can be seen that under these conditions, the K<sub>d</sub> value displays a significant magnitude with cadmium ions and lowest with the divalent nickel ions. In confirmation to the above results, the K<sub>d</sub> value acquired its lowest magnitude with the concentrated metal solutions as compared to the dilute ones.



**Figure 6:** The effect of addition of 80% v/v ethanol-water system without acetic on the  $K_d$  value for rinsing solutions having  $1 \times 10^{-5}$  M,  $1 \times 10^{-4}$  and  $3 \times 10^{-4}$  M ( $T=25^\circ\text{C}$ ).

### 3.4 Effect of the resorcinol dye together with ethanol on the $K_d$ value

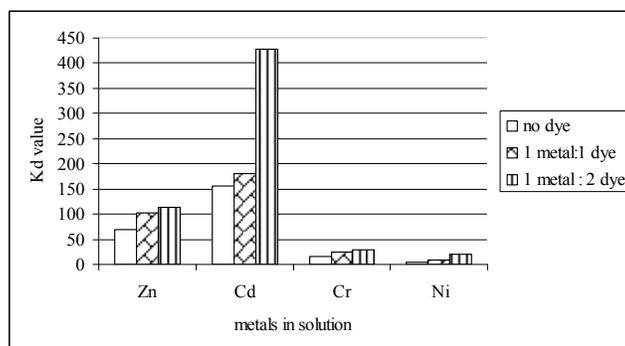


Figure 7a

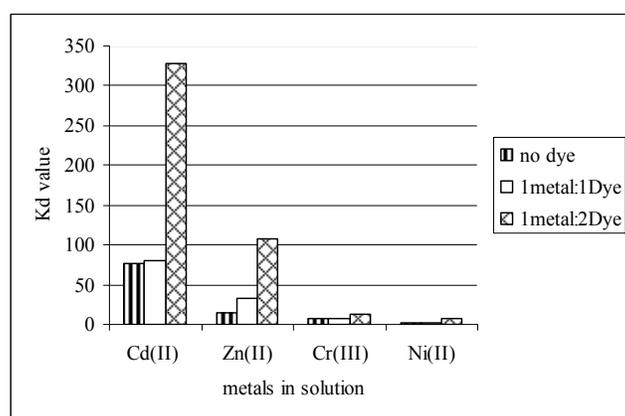
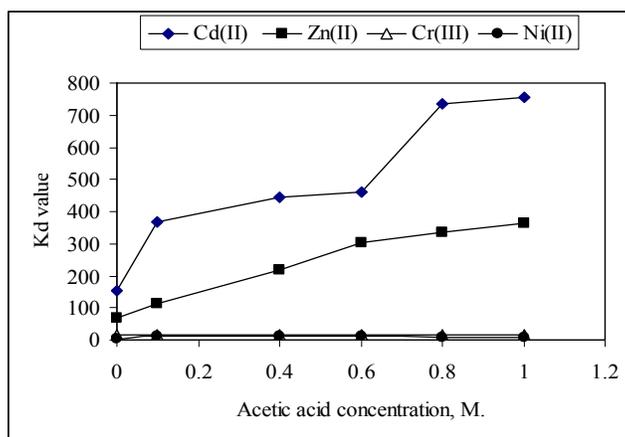


Figure 7b

**Figure7:** Effect of the resorcinol dye addition to the rinsing solution having  $1 \times 10^{-5}$  M<sup>+</sup> (7a) and  $3 \times 10^{-5}$  M<sup>+</sup> (7b) in presence of 80% v/v ethanol-water system without acetic acid ( $T=25^\circ\text{C}$ ).

Figure 7a shows the effect of addition of the dye in different molar ratios to dilute rinsing solutions ( $10^{-5}$  M) on the  $K_d$  value. It can be seen that the ratio 2 dye: 1 metal species displays the highest  $K_d$  value with cadmium ions

(438) and zinc ions (114). The  $K_d$  value acquired with chromium and nickel ions amounts to 14 and 7 respectively. Figure 7b shows the  $K_d$  value as affected by addition of the resorcinol dye to the rinsing solutions having  $3 \times 10^{-4}$  M in presence of 80% v/v ethanol-water system without acetic acid at 25 °C. It is seen that the dye increases the  $k_d$  value with cadmium ions (329) and zinc ions (107). On the other hand, resorcinol resin has a slight effect on  $K_d$  value acquired with chromium and nickel ions, 14 and 7 respectively. It is worthy to note that addition of the resorcinol dye in a molar ratio less than double the metal ions becomes less effective with all the investigated species. Also the effect of the dye on  $K_d$  value is pronounced with dilute solutions as compared to the relatively concentrated solutions. Figure 8 shows the results of similar set of experiments carried out with solutions having metal ion with higher concentration ( $3 \times 10^{-4}$  M) and acetic acid up to 1 mol. It is seen that  $K_d$  magnitude increases to 740 with cadmium, 380 with zinc, but slightly decreases to 15 instead of 19 with chromium and to 8.5 instead of 13.5 with nickel.



**Figure 8:** Effect of acetic acid concentration on the  $K_d$  value for rinsing solutions of  $3 \times 10^{-4}$  mol/L metal species in presence of dye: metal ions 2:1 molar ratio at fixed 80% v/v ethanol-water system. ( $T=25^\circ\text{C}$ )

### 3.5 Effect of pH value in presence of the dye-ethanol system on the $K_d$ value

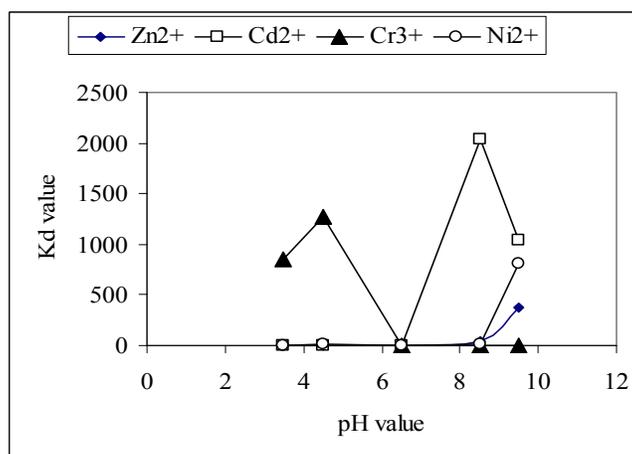


Figure 9a

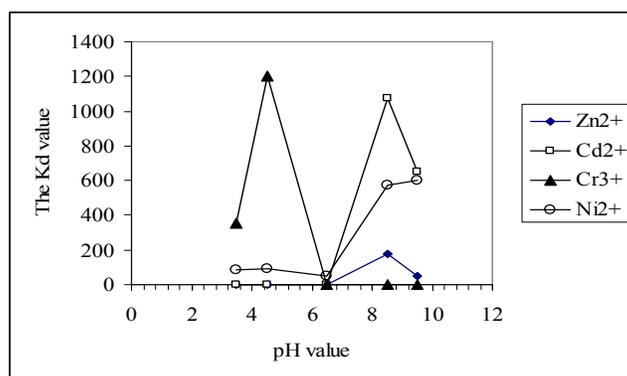


Figure 9b

**Figure 9:** Effect of pH value on  $K_d$  value with  $1 \times 10^{-4}$  mol/L rinsing solution (9a) and value with  $3 \times 10^{-4}$  mol/L (9b), ratio of the dye: metal ions = 2:1 at fixed 80% v/v ethanol-water,  $T=25^\circ\text{C}$ .

Figures 9a and 9b show the effect of pH on  $K_d$  value with rinsing solutions having metal ion concentration amounting to  $1 \times 10^{-4}$  mol (9a) and  $3 \times 10^{-4}$  mol (9b). The molar ratio of the dye: metal ion concentration was 2:1. Experiments were conducted in presence of 80% ethanol at  $T=25^\circ\text{C}$ . It is seen that in Fig.9a, the  $K_d$  value acquired with cadmium increases with the pH increase. A maximum  $K_d$  value is attained at pH 8.5. With more acidic solutions, scarcely soluble cadmium salts can precipitate. Chromium ions exhibit moderate  $K_d$  values in the acidic region ( $\text{pH} = 3.5\text{-}4.5$ ) and precipitate in more alkaline medium ( $\text{pH} \geq 6.5$ ). With zinc and nickel, the  $K_d$  values amount to 165 and 3050 at pH 9.5 respectively. In Fig 9b, a similar set of experiments was conducted using comparatively more concentrated metal solutions of  $3 \times 10^{-4}$  mol/L. Also the same dye: metal ion ratio (2:1) and in presence of 80% aqueous ethanol at  $T=25^\circ\text{C}$  were fixed. It is seen that the  $K_d$  value with cadmium decreased to 1076. With chromium, the  $K_d$  value decreased to 1200 instead of 1260 in the acidic medium (pH 4.5). With zinc and nickel, the  $K_d$  value dropped to 46 and 600 at pH 9.5. Figures 10a through 10d demonstrate the  $K_d$  values acquired with cadmium (10a), chromium (10b), nickel (10c) and zinc (10d) ions in the rinsing solutions. With any of these metal ions, the effect of pH value of the rinsing solution having ion concentrations  $1 \times 10^{-5}$ ,  $1 \times 10^{-4}$  and  $3 \times 10^{-4}$  mol/L on the extent of  $K_d$  value was studied. Experiments were carried out with 1 mol/L. acetic acid, 2:1 dye: metal ion ratio and at room temperature.

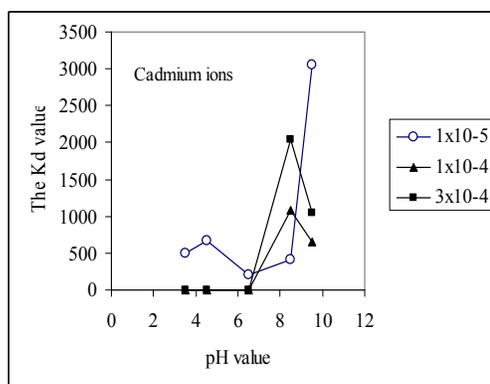


Figure 10a

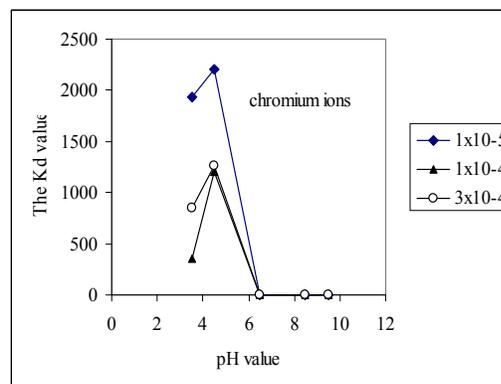
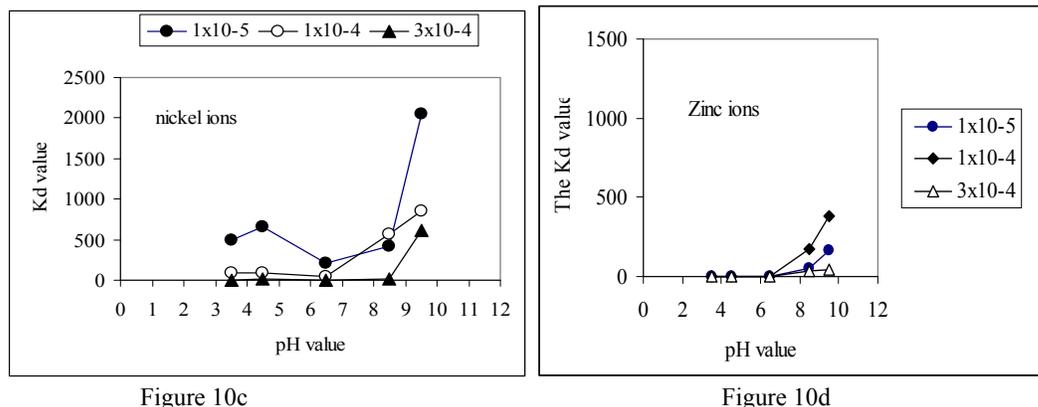


Figure 10b

It is seen that  $K_d$  values attained the highest values with cadmium (in alkaline medium) whereas it decreases in acidic solutions presumably due to scarcely soluble salts of cadmium precipitates. For one and the same pH value in the alkaline range up to 9.5, the  $K_d$  value decreases in the order chromium, nickel and zinc.



**Figure 10:** Effect of pH value of the rinsing solution on the extent of K<sub>d</sub> value with cadmium (10a), with chromium (10b), with nickel (10c) and with zinc (10d) with concentrations 1x10<sup>-5</sup>, 1x10<sup>-4</sup> and 3x10<sup>-4</sup> mol/L. (1 mol acetic acid, 2:1 dye: metal ion ratio at room temperature).

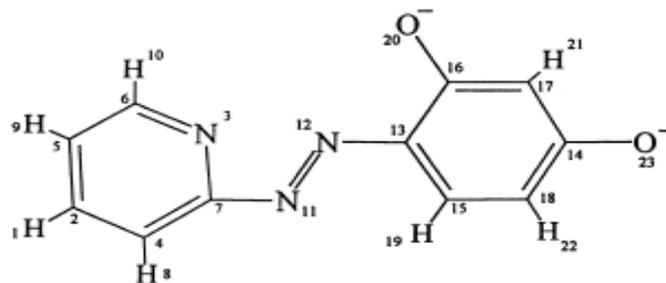
## 4. Discussion

### 4-a Capacity of the ion exchanger resin and dosage

In the present study, a strongly basic anion exchange resin Lewatit MP 600 was examined for its power to exchange some heavy metal ions from rinsing solution of electroplating industry. Also a resorcinol dye was used as a complexing agent by chelating metal ions. Fig. 1 shows the dye structure. The dye structure contains nitrogen atom (azonitrogen) furthest from the pyridine ring and ortho-hydroxyl oxygen (donor atoms) usually forms chelate with ligand (Roston [18]). The parameters that influence ion exchange capacity are the resin amount, the metal ions concentration, the dye dosage, pH of the solution and presence of organic solvents. Experiments of this work were manifested at 25°C. Results given in Fig.2 obtained with synthetic salt solutions shows that the partition coefficient K<sub>d</sub> is nearly insignificant as the anion exchanger does not adsorb positively charged ions. However, the decrease of K<sub>d</sub> value with the increase in the resin dosage is reasonable. In equation 2, increasing the m<sub>res</sub> fraction would bring about a corresponding decrease in the K<sub>d</sub> value provided that the adsorption capacity of the resin (ε<sub>r</sub>) as given in equation 1 is kept constant. The difference in the K<sub>d</sub> values exhibited with different metal ions is anticipated to the difference in the electro positive potential of their ions in solution (Weast and Astle CRC [19], d159-165). (Zn<sup>2+</sup> = +0.762V, Cr<sup>3+</sup> = +0.557V, Cd<sup>2+</sup> = +0.352V and Ni<sup>2+</sup> = +0.23V). The anion exchange resin uptake is only matched in presence of negatively charged species in the solution. Adsorption takes place when these species diffuse into the boundary layer at the resin-solution interface. Adsorption is affected on active sites on the resin surface. In this context, resorcinol dye reacts with the positively charged metal species to form negatively charged complexes that are adsorbed by the exchanger more easily. It becomes therefore understandable that addition of the resorcinol dye to the rinsing water is highly recommended to achieve significant adsorption of metal species and to increase the K<sub>d</sub> values to high extent.

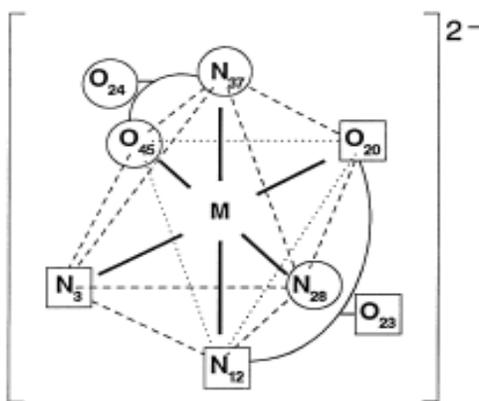
### 4-b Effect of the resorcinol dye and dosage

The 4-(2-Pyridylazo) resorcinol) dyestuff is one of the best chelating reagents for pre column complexation of many metal ions, because of its sensitivity, and solubility in water (Zhang et al., [20]).



The resorcinol resin di-anionic form,  $L_2^{2-}$ .

Most metal species form stable chelate with the resorcinol dyestuff. Absorption spectra investigation of the M-dye complexes shows a single band in the visible range with a maximum at 527-493.8 nm with zinc, 470 nm with cadmium, 471.6 nm with r and 525-527.2 nm with nickel (chart not given). The metal-dye complex shows an octahedral structure of  $ML_2^{2-}$  type, Fig.11.

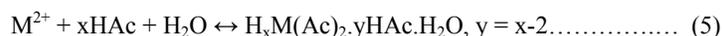


**Figure 11:** The Octahedral structure of  $ML_2^{2-}$  ( $M=Zn$  or  $Cd$ ) showing the possible attachment sites to the metal ion. (The atoms enclosed in a circle pertain to one ligand molecule and the atoms enclosed in a square pertain to the other one).

As a result, the metal-resorcinol chelate would form various protonated / de-protonated species. The metal: dye molar ratio is typically 1:2 or 1:1. Most of divalent metal ions form the 1:2 chelates with the resorcinol dye. Geary et al. [21] concluded that the dye acted as tridentate ligand towards bivalent metal ions. However, Stanely and Cheny [22], showed that no reference was made to the possibility that resorcinol could exist in a Trans – form. The electrostatic interaction and formation of complex compounds may be identified as the major adsorption mechanisms. Any of these mechanisms may work individually or in combination with the azonitrogen atom (furthest from the pyridine ring) and the ortho-hydroxyl oxygen for the adsorption of metal ions on the adsorbents. The difference in the adsorption behavior of  $Cr^{3+}$ -dye complexes on the resin indicates different surface interaction mechanisms (Deng and Bai, [23] undertook considerable effect between  $Cr^{3+}$  and the dye. The low value of partition coefficient obtained with Ni that indicates nickel forms less stable complexes whereby acetate ions may hinder complex formation. The anomalous behavior of nickel ions at pH 4.5 through 9.5 could be due to the formation of two complexes having different sorption characteristics. Cadmium displays higher selectivity for adsorption compared to nickel. Cadmium ions adsorbed on Lewatit MP 600 are retained without dissociation as its complex is hydrophobic. Zinc forms stable zinc acetate complex in the alkaline medium and this increases the adsorption extent on the resin. The  $K_d$  curves given in Figs 7a and 7b can be explained in terms of the gradual building-up of metal-dye complexes with increasing the dye dosage, the content of acetic acid and ethanol.

#### 4-c Effect of acetic acid addition

Korkisch and Urubey [24] reported that acetic acid reacts with some heavy metals ions to form acetate complexes increasing the  $K_d$  value. In the solvent phase, metals-acetic acid complexes  $H_xM(Ac)_{2+x}$  can be formed according to:



The complex metal-acetate  $H_xM(Ac)_2$  is further solvated by acetic acid molecules followed by water hydration. In the resin phase, the chloride counter groups will share to form negatively charged chloride-metal complex. The formation of the complex on the resin may take place according to the following reaction:



The increase in the acetic acid concentration would influence the  $K_d$  value because of transition of the dissociated species to join-paired and ion-paired species. The acid therefore contributes to the above equilibrium (eq. 4). It has been reported that such contribution was due to the enhanced formation and adsorption of metal-chloride or metal-acetate-chloride complexes. The formation of metal acetate complex was responsible for the high  $K_d$  values. The affinity of the metal ions for the  $RCl$  resin in acetic acid solutions is rather selective, De Crote et al. [25].

#### 4-d Effect of addition of ethanol

Ethanol is a less polar solvent with high dielectric constant magnitude ( $\epsilon_{Ethanol} = 33.8$ ). The dielectric constant magnitude of acetic acid is low ( $\epsilon_{HAC} = 6.2$ ) compared to ethanol. The effect of ethanol addition in presence of water-acetic acid (ternary system) on the  $K_d$  value follows the same role displayed by the acetic acid effect. The presence of ethanol in the aqueous system enhances the extent of complex formation. Inglezakis and Loizidou [14] showed that the enhanced  $K_d$  value was attributed to the dehydration effect particularly with the ions having larger ionic radii ( $Cd = 0.97 \text{ \AA} > Zn = 0.74 \text{ \AA} > Ni = 0.69 \text{ \AA} > Cr = 0.63 \text{ \AA}$ ). Ethanol decreases the dielectric constant of the ethanol-acetic acid-water system to low value helping formation of negatively charged complexes. It is assumed that the electrostatic interaction, surface complexation, and ion-exchange mechanisms may be identified as the main adsorption mechanisms that work individually or in combination for the adsorption of metal ions on the adsorbents in a good agreement with Deng and Bai [22].

#### 4.5 Effect of pH value

The pH value of industrial rinsing wastewater controls the sorption of metal species. Variation of adsorption in presence of 1 mol acetic acid and different pH values may suggest that the adsorption capacity is a pH-dependent process. There was no adsorption uptake of  $Cr^{3+}$  on Lewatit MP 600 resin at  $pH < 3.5$ . Adsorption increases drastically as the pH increased to 4.5. Due to hydrogen ion competition at low pH values, the  $Cr^{3+}$  uptake was small [Da Fonseca et al., [26], Vijayaraghavan et al., [27] and Unlu and Ersoz [28]]. This is in agreement with the work reported by Unlu and Ersoz, [28], Alvarez-Ayuso et al., [29], Abollino et al., [30], Tuzen et al., [31], Farajzadeh and Monji, [32].  $Ni^{2+}$ -acetate complex forms stable compounds with the resorcinol dye in alkaline medium pH (8.5-9.5). At pH 9.0 two hydroxyl-acetate complexes are found with different sorption characteristics. At more basic medium, scarcely soluble Ni salts  $M^{x+}(OH)_x$  would precipitate. Adsorption of cadmium-acetate-dye complex was higher than Ni and amounts to 10 times of Zn. At  $pH = 8.5$   $Cd$  complex has a hydrophobic property that helps adsorption. Experimental results show that resorcinol has a low affinity towards  $Zn^{2+}$  ions in different pH values. It follows that the extent of adsorption is in the order  $Cd > Ni > Cr >> Zn$ . 4.6 Stripping of the metal species from the loaded resin Stripping is a reversible process of opposite capacity to the adsorption step. Stripping of the metal species from the loaded organic phase was conducted with 4 M HCl solution. Results revealed that elution takes place more readily in the order  $Zn > Ni > Cd > Cr$ . Separation of the eluted metals originally present in the rinsing water can be matched in the same ordering. Cadmium separates from both Cr and Ni solutions at pH 4.5. Chromium is separated from Ni at pH 8.5 whereby separation of zinc is carried out at  $pH \geq 9.5$ . The metals so separated are in chloride form. Other metals value can be prepared by converting the chloride salt to insoluble hydroxide (using ammonium hydroxide). The latter is a base for preparation of other salts.

## 5. Conclusion

This study shows that Lewatit MP 600 can be used for purifying industrial rinsing wastewater and subsequent separation of chromium, zinc, cadmium and nickel species. An organic resorcinol dye was used as a complexing agent. The organic nature of the mobile phase enhances the electrostatic interaction of the analyte ions and the sites accessible for adsorption. The electrostatic interaction and formation of complex compounds may be identified as the major adsorption mechanisms. Any of these mechanisms may work individually or in combination with the azonitrogen atom (furthest from the pyridine ring) and the ortho-hydroxyl oxygen for the adsorption of metal ions on the adsorbents. However, this effect is relatively dependent on the properties of the solvent. The assumption that the observed retention simply enhanced ion exchange is verified by the effect of the pH, buffer type and metal ion concentration, which are as expected for a simple ion-exchange system. Stripping is reversible process of opposite capacity to the adsorption step. It takes place by hydrogen atom donor compound such as hydrochloric acid.

## 6. References

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