Synthesis and Characterization of the Amide Resin R3A2-20.7 n.H its Performance for removal of Ni(II) & Cu(II) from plating waste effluent

Dr.Gunjan.B. Dave[1]
[1]*Shri Kokilaben Karsanbhai Patel Girls Science College,Nanikadi (North Gujarat), India.*
gunjandave84@yahoo.com

Abstract :

A new polymer based resin containing amine group was synthesized. Amine group has been incorporated onto copolymer by a modified polymerization method of functionlisation of polymers. Amide resin (R3A2-20.7 n.H) canselectively separate heavy metal ions like Ni2+andCu2+from industrial plating wasteeffluent. The resin was characterized by FTIR and thermodynamic parameters. The distribution coefficient of metal ions at different pH was studied using batch adsorption method.

Keywords: *Amide Resin (R3A2-20.7 n.H), Adsorption, pH, Desorption, Metal ions removal*

1. Introduction

Copper and nickel are the heavy metals which have been widely used in electroplating industry. The typical form of copper and nickel which are used in plating is the divalent nickel and copper. The work on resin by Cooper (1987) and Parker (1980) have reported that wastewater contaminated with divalent nickel and copper is discharged to waterways without adequate treatment pollutes soil and water resources Electroplating operations form part of large scale manufacturing plants (e.g. automobile, cycle, engineering and numerous other industries) or perform as small scale industries They are spread across the entire country with significant concentration in several states like Punjab, Haryana, part of U.P., Maharashtra, Karnataka, Andhra Pradesh, Tamil Nadu and West Bengal. Electroplating is considered a major polluting industry because it discharges toxic materials and heavy metals through wastewater (effluents), air emissions and solid wastes into the recipient environment. Heavy metals like nickel and copper are harmful to humans and other living organisms. WHO demonstrating in 1982 that inhaling of divalent nickel and copper causes an increase in the incidence of lung cancer. Moreover, soluble nickel compounds are carcinogenic, giving rise to cancers of the nasal cavities, lungs and other organs such as stomach and kidney. Dadhich et al. (2003) have shown that nickel is largely present in the wastewater of electroplating, motor vehicle and aircraft industries. Rao et al. (2001) have reported that Acute nickel (II) poisoning causes dizziness, headache, nausea and vomiting, chest pain, dry cough and shortness of breathe rapid respiration, cyanosis and extreme weakness. WHO (1982) has suggested that the maximum amount of nickel in drinking water should be 0.1 mg / L^3 but in many electroplating effluent it is as high as 50 mg / L. Sreenivasulu and Komal Reddy (1998) have reported that sufficient requirement of body is 2 mg / L of copper but excess level of copper may result in damage of lever Copper is much toxic to aquatic organisms even its small amount. It is strongly required to remove from waste effluent in maximum amount

Bansal et al. (1988) investigated adsorption (especially activated carbon adsorption) appears to have the least adverse effects of health and environment. According to Annual book of ASTM standards (2001) adsorption includes a broad range of carbon aqueous materials at a high degree of porosity and large surface area which facilitated to removel of toxic, biodegradable and non-biodegradable substances from waste water. It is attractive as it can treat waste water to acceptable quality suitable for reuse. The removal efficiency of synthetically prepared resin towards nickel (II) and copper (II) was carried out in the present study. Various parameters including adsorbate dose, pH, contact time and concentration have been investigated intensively.

2.Material and methods

2.1 Resins

Acrylonitrile, methylmethacrylate and

ethyleneglycoldimethacrylate were used as monomer which were functionalized by amination to prepare amide resin and after finishing it was used for the removal of Ni^{2+} and Cu^{2+} from plating waste water. Monomer of resins are purchased from local chemical market of Ahmadabad

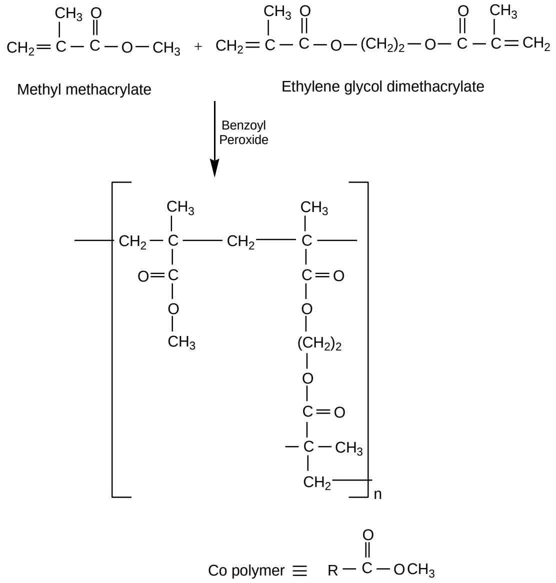
Synthesis of macroporous copolymers

Cross linked copolymers of methylmethacrylate-ethyleneglycol dimethacrylate and 4-vinyl pyridine- divinyl benzene were prepared by suspension polymerization. In this technique, polymerization is performed in an aqueous phase which containing the stabilizer. The mixture having the monomer, the cross-linker and the initiator dispersed in diluents is added into a flask containing the suspension medium. The polymerization is carried out at elevated temperatures for several hours resulting in polymeric micro beads obtained by filtration or centrifugation and washing. The polymerization was done in a three neck round bottom flask equipped with a mechanical stirrer, thermometer and reflux/distillation condenser. Required amount of saturated sodium chloride solution containing 2 % (w/v) starch as the suspension stabilizer was heated to 100 ^{0}C and then the temperature was brought down to 70 ^{0}C and mixture of required amounts of monomer mixture, diluents and initiator (1.0 wt % of benzoyl peroxide with respect to monomers) was added with controlled stirring. The ratio of reaction mixture (monomer plus diluents) to suspension medium was maintained at 1:7 w/v. The copolymerization was carried out initially at 70 ^{0}C for 1 hour, at 80 ^{0}C for 2 hours and then at 95 ^{0}C for 2 hours. The copolymer beads were recovered by filtration. They were thoroughly washed with tap water followed by warm water to remove the suspension stabilized. Then products beads were extracted with acetone in a soxhlet apparatus to remove trapped diluents or unreacted monomers and finally dried at room (Figure 2.1.1) temperature for 24 hours. The copolymer beads having –30, +52 B.S.S. mesh size were selected for further study in polymerization.

Preparation of weak base anion exchangers from MMA-EGDMA copolymers

Amination;

Amination reaction was done by use of triethylenetetramine. The copolymer beads thus prepared converted to weak base resin by this treatment. Anion exchange resins, produce by amination with triethylenetetramine contain primary ($-NH_2$) and secondary (-NH) amine sites. Resins originally having white color became pale yellow after the completion of amination. The polymer volume changed to nearly two times after amination. The probable reason is the introduction of ***triethylenetetramine moiety in the*** polymeric matrix. The resin particles also become much denser than polymers because of hydrophilicity of resins due to the introduction of amine groups. Figure given below shows the reaction scheme of amination and probable structure formula of this weak base resin.



Amination of Methylmethacrylate- Ethylene glycol dimethacrylate copolymers

2.3 FT-IR spectra

The IR spectra of MMA-EGDMA copolymers. The IR spectrum shows strong characteristic band around 1732 and 1147 cm-1 corresponding to >C=O and –OCH3 stretching respectively in the pendent group (-COOCH3) of methylmethacrylate and EGDMA. The spectra shows absorption in the 1500-700 cm-1 range, which results from C-O stretching vibration (1270-990 cm-1), C-H bending vibration (1450-1350 cm-1) and CH2 rocking vibration (810-7590 cm-1) Data corresponding to Figure 1 &2 [111].

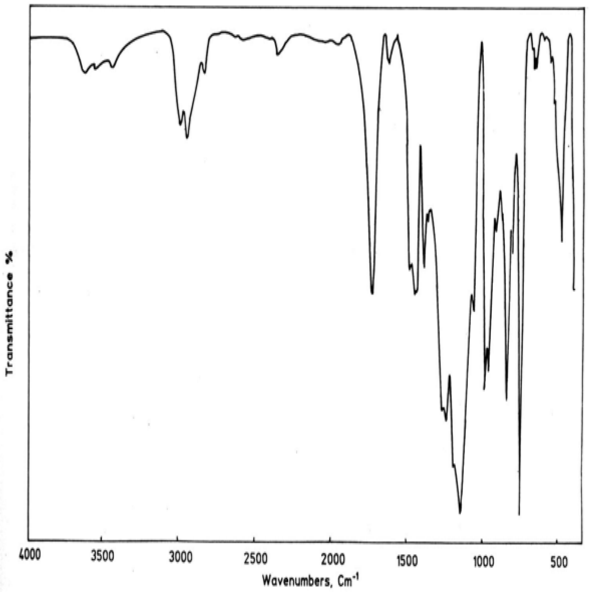


Fig.1.IRspectra of Methylmethacrylate Ethylenglycol dimethacrylatecopolymer

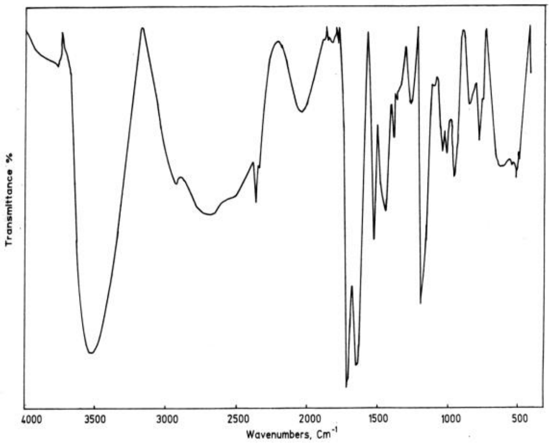


Fig.2. IR spectra of Aminated Methylmethacrylate-Ethylene glycol dimethacrylate copolymer

The IR spectra of weak base anion exchanger resin is shown in Fig. 2. The spectra shows broad absorption band at 3400-3500 cm^{-1} due to amide (-N-H) and (-O-H) groups [117]. The absence of band due to –OCH3 group and the carbonyl (C=O) stretching are observed at about 1633 cm^{-1} due to amide group. This clearly indicates the attachment of oligo ethylene functionality to the methacrylate unit by the elimination of methanol from MMA-EGDMA copolymer upon amination.

3. Results and discussion

3.1 Characterization of Calibration Curve

Calibration curve was prepared by using different known concentrations of copper and nickel solution. The absorption of these solutions were measured by UV-VIS spectrophotometer with PC. The standard calibration curve was prepared by plot a graph of Absorption Vs Concentration.

3.2 Analysis of metal ions

Nickel (II) and Copper (II) absorbance were estimated using spectrophotometric method with the help of UV-VIS spectrophotometer with PC. The absorption of nickel (II) and copper (II) were measured at Wavelengths 400 nm and 710 nm respectively.

3.3 Isotherm procedure

Minimum adsorption contact time have been calculated before isotherm studies. Each experiment comprised six replicate 100 ml glass bottles having stoppers contains appropriate amount of resins and 50 ml of adsorbate solutions of selected concentrations metal ions. Mixtures were stirred in a rotary shaker (orbitek) at constant temperature 33 ^{0}C. After the attainment of equilibrium the contents of each bottles were filtered through Whatmann filter paper no. 41 with the first 10 ml discarded. The filtered samples were then analyzed for unadsorbed metal ions. The equilibrium adsorption data were then fitted with Freundlich and Langmuir isotherm equations.

Langmuir : $qe = KLCe /(1 + bCe)$

Freundlich : $qe = KR\,Ce / (1 + Ce\beta)$

where qe is the adsorption capacity in mg /g, Ce is the equilibrium concentration , KL and b are Langmuir constants, qm is the Langmuir monolayer adsorption capacity and KR, bR and β are Freundlich isotherm constants.

3.4 Effect of initial Concentration

Concentrations Ni^{2+} and Cu^{2+} were selected in the range 5-6 to 30-31 mg L^{-1} for the adsorbent of two different resin (at pH 6.0). Experiments were carried out using 500-550 mg of resin with different concentrations of metal ion (5 - 40 mg L^{-1}). It was found that the metal amounts retained were almost stable in this concentration range for nickel and copper for two different resins. The maximum adsorption 81 % was reported for 10 mg L^{-1} concentration. Adsorption of Ni (II) and Cu (II) from Aqueous Solution:

3.5 Effect of pH (Method)

In order to find out the effect of pH for maximum removal of metals, different samples of metal ions containing different pH were prepared using NaOH and HCl and Perchloric acid. All these samples prepared are of the same concentration

3.6 Desorption Studies(Method)

To fine out the recovery of metals ions its require to elucidate the nature of adsorption processes. After the completation of experimental session using selected doses of resins. Loaded resins were separated and washed gently with distilled water to remove unabsorbed species.

3.7 Characterization of the Resins

Table 1. Characteristics of Amide group containing Resin.

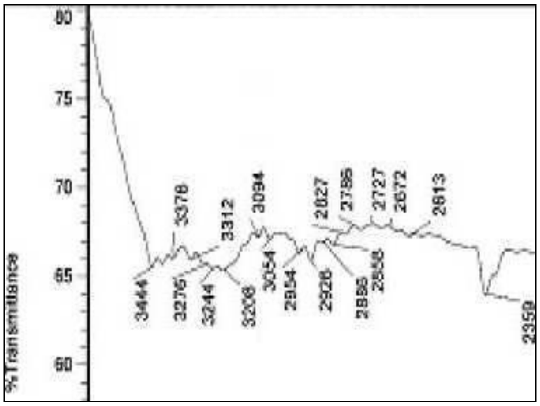


Figure .3. FT-IR spectrum of the Resin

For each adsorption system, the data were fitted to the three isotherms equations and the results are given in Table–2. [Conditions: adsorbent dose 0.1 gm/50 mL of adsorbate solution; initial concentration of metal solutions $Q = 15 - 100$ mg / L for Ni and 20 -100 mg / L for Cu] All the curves were of L type under Giles classification.

According to Treybal (1980) it can be seen that *n* values between 0 and 1 represent beneficial adsorption. Indeed, the *n* values found for all the adsorption systems fall in this range. Manivasakam et.al. (1984) have reported that the Langmuir constant *b* is a measurement of adsorption intensity and the parameter q_m is a measurement of adsorption capacity. Adsorption capacity of the adsorbents toward metal ions decreases in the order Ni(II) < Cu(II) respectively [values in Table 2].

According to conney (1999) in all the studied systems, RL values were comprised between 0 and 1 (values not listed) indicating favorable adsorption of all the metal ions on the

4. Conclusion

On the basis of the experimental data and the results reported, it is concluded that for ion exchange

activated carbon.

3.9 Effect of pH(Experimental)

The effect of pH in external solutions on resin extent are presented in Figure- 2. adsorbent doses : 0.1gm / 50mL, Ci= 50 mg / L).

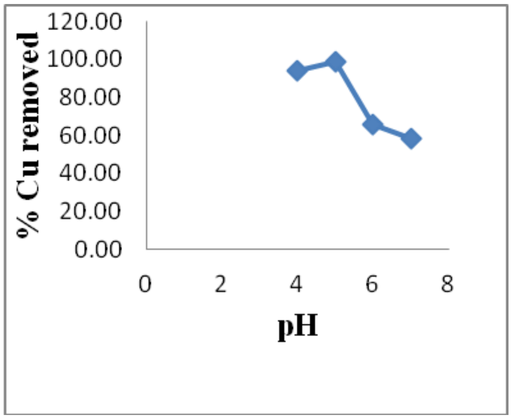


Figure 4. Effect of *pH on adsorption of copper(II).*

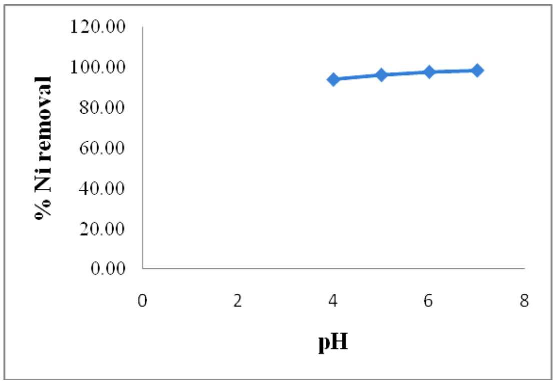


Figure 5. Effect of *pH on adsorption of nickel(II).*

3.10 Desorption Studies (

.

An attempt has been made to regenerate the adsorbed metal ions with water, 1 M NaOH and 1 M hydrochloric acid solution as regenerating agents by the method reported earlier Johnson (1990). The results indicate that the metal ions are adsorbed by the ion-exchange mechanism on the surface of the resin.

column study column should be minimum size of 55 cm length and 2.2 cm diameter to get better results. In comparison of the two resin, 3.0 gm. amount of resin and sufficient bed volume in column for 1 hour of contact time with copper (II) solution of pH 6.0, copper removal efficiency of (Amide resin) R3A2-20.7 n.H resin is reported very high in comparison with the Dowex M 4195 resin. It was also observed that the copper removal efficiency of R3A2-20.7 n.H resin increases with the increasing in the concentration of copper (II) solution. The work described shows that the functional group amine containing resin can be hopefull to be used for the effective removal of metal ions Cu (II) and NI (II) from the solution. Amine and bispicolyl amine have possessed good textural and chemical properties. Increase in the pH of the solution resulted in greater retention of metal ions in calibration curve. The adsorption processes were found endothermic. Thermodynamic parameters like effect of resin dosage, effect of pH, effect of contact time and effect of concentration were evaluated.

Acknowledgement

Authors are thankful to Science college, Pilvai, affiliated to Hemchandrachrya north Gujarat university, Patan For kind support.

References

[I] Annual Book of ASTM Standards, 2001. Refractories; Activated Carbon; Advanced Ceramics. Volume 15.01.

[II] Atkins P. W. and Julio de Paula, 2002. Atkins' Physical Chemistry, 7th Ed., Oxford University Press, Inc. New York, 989.

[III] Bansal R. C., Donnet J. B. and Stoeckli F., 1988. Active Carbon, Marcell Dekker, New York.

[IV] Bandosz T. J., Jagiello J. and Scharwarz J. A., 1996. Langmuir, 12, 6480-6486.
Cooper W. J., 1987. Chemistry in Water Use., 1, 265.

[V] Conney D. O., 1999. Adsorption Design for Wastewater Treatment, CRC Press LLC:Boca Raton, FL.

[VI] Dadhich A. S., Beebi S. K., Kavitha G. V. and Chaitanya K. V. K., 2003. Asian J. Chem., 15, 772-780.

[VII] Giles C. H., MacEwan T. H., Nakhwa S. N. and Smith D. J., 1960. Amer. Chem. Soc. 4, 3973-3993.

[VIII] Ho Y. S. 2001. Adsorption, 7, 139- 147. Ho Y. S. J. 2003. Colloid Interface Sci., 262, 307-308.

[IX] Johnson B. B., 1990. Environ. Sci. Tech., 24, 112-118.

[X] Khalid N., Ahmed S., Kiani S. N. and Ahmed J., 1998. Sep. Sci. Tech., 33, 2349- 2362.

[XI] Khalid N., Ahmed S., Kiani S. N. and Ahmed 1999. J., Sep. Sci. Tech., 34, 3139-3153.

[XII] Kapadia M. J., Farasram R. P., Desai D. H. and Bhatt M. M., 2000. Ind. J. Env. Prot., 20, 521- 528.

[XIII] Maria J. M., Adriana A. M., Dolars Balaguer and Miquel Rigola. 2002. J. Chem. Technol. Biotechnol., 77, 825-833.

[XIV] Manivasakam N., Physiochemical Examination of Water, ewage, 1984. Industrial Effluents, Pragati Prakashan, 161- 163.

[XV] Mendham V. J., Denny R. C., Barnes J. D. and Thomas M. J. K., 2002. Vogel's Textbook of Quantitative Chemical Analysis, 6th Ed.,Pearson Education (Singapore) Private Ltd., 668.

[XVI] McKay G., Otterburn M. S. and Sweeny A. G. 1980. Wat. Res., 14, 21- 27.

[XVII] Parker S. P. (Editor), 1980. Encyclopedia of Environmental Sciences, 2nd Ed., McGraw- Hill, New York.

[XVIII] Rao M., Parvate A. V. and Bhole A. G., 2001. Poll. Res., 20, 669-675.

[XIX] Sreenivasulu S. and Komal Reddy, 1998. Ind. J. Environ. Prot., 18,687-693.

[XX] Snell F. D., Snell C. T. and Snell C. A., 1959. Colorimetric Methods of Analysis, Volume II . A. D Van Nostrand Company Inc. Princeton, New Jersey, 67-69.

[XXI] Treybal R. E., 1980. Mass- Transfer Operations, McGraw-Hill Publishers, New York.

[XXII] Thirunavukkarasu O. S., Viraraghavan T., Subramanian K. S. and Tanjore S. 2002. Urban Water, 4, 415-421.WHO,1982

[XXIII] Applications of Guidelines for Drinking Water Quality, Document EHE/EHC/81.27