# Preparation and characterization of cellulose based methacrylic acid resin for the purpose of wastewater treatment

**Dinesh, Sankhla Manisha and Singh A.V.***
Department of Chemistry, J.N.V. University, Jodhpur, Rajasthan, INDIA
*areshvikram04@rediffmail.com

***Abstract***

*In raising substantial concerns, micropollutants occur in water resources worldwide due to many causes. As a result, this has adverse impact on ecosystem especially aquatic life and in turn on humans. Ion exchange method is the best method as polymeric resin which has effective alternative adsorbent. This adsorbent has high porosity and accessibility, significant adsorption sites and stable chemical properties. Unmodified cellulose incorporated with the methacrylic acid to make it modified cellulose increases efficiency for the adsorption of heavy metal ions.*

*In turn, modified methacrylic acid (CMAA) resin has good adsorption capability specially for environmentally toxic metal ions: lead($Pb^{2+}$), copper($Cu^{2+}$), chromium($Cr^{3+}$) and cadmium($Cd^{2+}$). Prepared resin showed higher retention of heavy metal ions by batch and column method respectively. Sorption equilibrium is found when there is effect of temperature on capacity of a cation exchanger. This study contains the preparation or adsorption of methacrylic acid on cellulose to treat the industrial effluent. Characterization of adsorbent was performed by FTIR and thermogravimetric analysis. Experiments were performed at different pH, concentration of metal ion, contact time etc.*

**Keywords**: Heavy metal ions, Industrial Effluent, Cellulose methacrylic acid, FTIR.

## Introduction

The advantage of preparing cellulose based methacrylic acid resin as a water remediation technique is that it is very cost effective, less amount of energy is required and resin can be regenerated which is very economical. If resin is maintained efficiently, it can be used for several times.

Heavy metals like mercury, lead, tin, cadmium, selenium, chromium and arsenic are introduced to the environment by different human activities and getting deposit in surrounding water bodies and soil slowly.[2,5,12,16]. The accumulation of heavy metals may constitute a public health problem and can cause brain damage, poisoning and can initiate cancer, when found above tolerance level[7,11,18,19]. Ion exchange method has become most effective method in treatment of industrial wastewater which helps in adsorbing heavy metal ions effectively[9]. Matrix of polysaccharide having varieties of functional selecting groups also showed exclusion or removal of heavy metal ions from aqueous solution of Industrial waste water[3,13]. Another type of adsorption of metal ions by ion exchange method is a green analytical method used in conventional liquid extraction technique, though it does not use chlorinated organic solvents[14].

The conventional technologies include physical, chemical or biological methods[1,4,8]. Physical methods are sedimentation, screening, filtration and membrane separation. Chemical methods are chemical precipitation, coagulation, ion exchange, adsorption, neutralisation, solvent extraction. Biological methods are aerobic and anaerobic. Among these, adsorption method is known to be best as it is an economical effective and eco-friendly technique for the contamination of water or wastewater treatment. Adsorption is basically a mass transfer process used to bound metal ions from solution to the sorbent in solution.

## Material and Methods

**Materials and Methods:** Cellulose powder was acquired from Ases Chemicals, Jodhpur, India. Epichlorohydrin and methacrylic acid was purchased from Sisco Chemical Industries, Mumbai, India. Sodium hydroxide and dioxane were used from Sarabhai Chemicals, Baroda, India.

**Synthesis of Cellulose Methacrylic Acid Resin:** The cellulose methacrylic acid resin was synthesized in two steps. In first step, epoxypropyl ether of cellulose in alkaline medium was synthesized. Epoxypropyl ether of cellulose was synthesized by taking cellulose powder (16.2 g), slurried it with dioxane in round bottom flask and 4 g (0.1mol) of 50% of aqueous solution of sodium hydroxide was poured to make it alkaline (pH = 9.5). After stirring for 1 hour, epichlorohydrin was added drop by drop and stirring was continued for 4 hours at temperature $60^0$ C. In second step, the product epoxypropyl ether of cellulose undergoes reaction with methacrylic acid (8.60g, 0.1mol) and stirring was continued for 5 hrs at temperature $65^0$ C . The resultant resin was filtered under vacuum and washing was performed with 90% methanol and HCl to purify the resin. The CMAA resin was light brown fine powder. The yield of resin was 25.6 g.

**FT-IR Characterization:** For FT-IR characterization, Perkin Elmer model 2380, Atomic Absorption Spectrophotometer was implemented which gives the data related to band region and functional group stretching frequency. First, ungrafted or unmodified cellulose was analysed and it showed band of broad nature in the 3200 $cm^{-1}$ and 3500 $cm^{-1}$ regions with characteristic --OH (Functional group) stretching frequency. After grafting of methacrylic acid on cellulose (CMAA) resin, it showed a characteristic band at 1731$cm^{-1}$ which confirmed the formation of methacrylic acid resin grafted cellulose. Results were anomalous to the stretching vibrations of carbonyl group.

**Thermogravimetric Analysis:** To perform dynamic measurement, thermogravimetric analyser (Dupont 951, USA) was set up at 20$^o$ C/minute heating rate. Necessary condition for this analysis was attained by measuring the resin sample and then dried in the desiccator. The CMAA resin got stable at 398$^o$ followed by rapid degradation.

**Column operation/analysis:** In synthesis of cellulose methacrylic acid resin, metal ions were recovered by analysing column method. Apparatus required in this method is glass tube of 1.6 cm internal diameter and 18 cm height in which 8 cm resin was embedded. Peristaltic pump is used to control the flow rate. Metal ions of binary mixture are separated on the concept of selective elution followed by removal of least traces of unadsorbed ions with distilled water.

## Results and Discussion

**Distribution coefficient ($K_d$) of metal ions:** The pH has a strong effect on the distribution coefficient ($K_d$) of metal ions. The perusal of the results showed that the distribution coefficient value first increases and decreases with increasing pH. The best results were obtained at pH 6.

**Effect of pH:** Different parameters were taken into consideration, out of which wide range of pH shows increasing and decreasing distribution coefficient values of metal ions. This pH became important point to describe, as it affects the metal ion's solubility, it also affects the adsorbent's degree of ionization at the time of reaction and counter ion concentration on the functional group of adsorbent. The effect of pH on relative activity was determined in the pH range of 2 to 8 shown in table 1 and 2.

**Table 1**
**The Characteristics of Neelkanth Steel Industry, Jodhpur**

| **pH** | 3.9 | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Appearance** | Green Yellow | | | | | | | | | |
| **Total Hardness** | 972 | | | | | | | | | |
| **Metal ion** | $Cu^{2+}$ | $Zn^{2+}$ | $Pb^{2+}$ | $Cd^{2+}$ | $Ni^{2+}$ | $Mg^{2+}$ | $Cr^{2+}$ | $Ca^{2+}$ | $Fe^{2+}$ | $Co^{2+}$ |
| **Concentration (ppm)** | 1.30 | 8.42 | 0.93 | 0.15 | 0.54 | 21.1 | 0.96 | 88.7 | 1.79 | 1.28 |
| **Others anions(ppm)** | Fluoride=0.24; Sulphate=740; Cyanide=0.03 | | | | | | | | | |

**Table 2**
**Distribution coefficient (Kd) of metal ions**

| pH | Pb (II) | Cd (II) | Zn (II) | Cu(II) | Fe(II) |
|---|---|---|---|---|---|
| 2.0 | 07.13 | 24.36 | 18.23 | 22.78 | 23.32 |
| 3.0 | 10.34 | 26.57 | 23.76 | 34.25 | 45.61 |
| 4.0 | 14.76 | 29.17 | 30.23 | 28.46 | 52.65 |
| 5.0 | 26.38 | 64.24 | 52.86 | 94.16 | 174.32 |
| 6.0 | 81.11 | 114.10 | 139.52 | 242.24 | 747.65 |
| 7.0 | 21.31 | 25.62 | 31.28 | 40.23 | 49.77 |
| 8.0 | 09.47 | 11.15 | 13.74 | 16.92 | 21.83 |

**Table 3**
**Percentage removal of metal ions from the industrial effluent by CMAA Resin**

| pH | Pb (II) | Cd (II) | Zn (II) | Cu (II) | Fe (II) |
|---|---|---|---|---|---|
| 2.0 | 32.17 | 57.31 | 63.42 | 67.56 | 73.85 |
| 3.0 | 56.64 | 67.49 | 72.39 | 71.48 | 80.13 |
| 4.0 | 58.99 | 76.35 | 78.92 | 89.90 | 84.68 |
| 5.0 | 70.41 | 83.89 | 85.73 | 92.38 | 96.97 |
| 6.0 | 85.38 | 94.62 | 96.16 | 97.11 | 99.12 |
| 7.0 | 52.24 | 74.56 | 71.96 | 79.95 | 82.11 |
| 8.0 | 42.34 | 51.67 | 53.27 | 58.79 | 69.27 |

The persual of research shows that Kd value first increases and then with the increasing pH value, it decreased. The best results of up taking free metal ions occur at pH value 6 and as described above, results are decreasing at higher pH.

**IEC of CMAA Resin:** Final yield of synthesised resin cellulose methacrylic acid is 1.69 meq/g.

## Conclusion

Insoluble cellulose methacrylic acid resin was synthesized to obtain the desired objective of separation of heavy metal ions from wastewater successfully performed in the laboratory. Experimental method shows that 0.1 g of resin is sufficient for the treatment of 1litre of wastewater because number of binding sites were available on the surface of CMAA resin. Finally, CMAA resin was ready to be applied in the wastewater treatment for the removal of heavy metal ions.

The complete synthesis of CMAA resin is eco-friendly and beneficial to human society. Modified cellulose methacrylic acid can be applied for wastewater treatment to make water free from hazardous heavy metal ions like Pb(II), Cd(II), Zn(II), Cu(II) and Fe(II).

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