METAL REMOVAL WITH CARBOXYMETHYL CHITOSAN USING SMALL COLUMNS

Zeenat M. Ali* Shuaib M. Laghari **, A. Jabbar Laghari*** M.M. Tunio****

ABSTRACT

Chitosan has reactive amino (NH_2)& hydroxyl (OH) groups on its skeleton, which could be used for chemical modifications under mild reaction conditions to alter its properties. In present work the alkylation method was opted for the preparation of carboxymethyl chitosan. The characterization of the compound was carried out via scanning electron microscopy, energy dispersive x-rays and fourier transformation infrared (FTIR) techniques. Five small columns were prepared each contained 2 gram carboxymethyl chitosan. The columns carried copper (lI), zinc (II), chromium (IIl), iron (II) and nickel (II) solutions having concentrations of 10-100 µg/L. When compared the order was Cu>Zn>Cr>Fe>Ni. The removal efficiency of over 86.4% - 95.1% and recovery of 100% was observed from wastewater for copper (132 mg/L), zinc (171 mg/L), chromium (118 mg/L), iron (353 mg/L) and nickel (96mg/L).

Key words: *efficiency, chitosan, columns, solution*

1. INTRODUCTION:

Many water-soluble derivatives have been prepared by quaternization or by introducing carboxyalkyl groups as carboxymethyl, carboxyethyl, carboxybutyl water-soluble Polymers in macromolecular chain of chitosan.In present work the carboxymethyl chitosan was prepared by modified direct alkylation method [**1**], because it utilized monochloroacetic acid for preparation of chitosan derivatives under optimum reaction conditions by soaking it into alkaline solution of pH 8–8.5 where only the amine groups were activated. The carboxymethyl group in present research work it was derivatized through O-chitosan [Fig. 1]. Wang et al [2]investigated crude oil for possiblemetal removal capacity by carboxymethyl chitosan using microwave technique. According to results the removal efficiencies of nickel and vanadium were 69.79%-93.66% at 60 °C with 500 mg/L dosage. Kannamba et al [3] reported preparation of cross linked xantate-chitosan for removal of Cu (II).Parameters for Cu(II) such as temperature, contact time,concentration, and pH wereexamined. Sepehran [4] et al reported Cu (II) and Ni(II) removal efficienciesfromsolutionsusing chitosan and modified chitosan at two values; pH 2.8 and pH 4.8 with 20 minute and 18 hours contact time. Gandhi et al [5] enhanced the sorption capacity of chitosan throughchange in beads of chitosan in order to remove copper. The Physical parameters studiedfor copper suggested nature if endothermic could follow Freundlich isotherms.Emaraa Adel [6]worked on derivatives ofchitosan for uptake of copper Cu(II) and concluded 0.461-0.572mmol/g concentration intake capacity at pH 5.6. Whereas polymer cinnamoylisothiocyanate examined wasbetter incomparison to other polymers for (Fe(lll), Cr(lll),Co(ll),Ni(ll)).

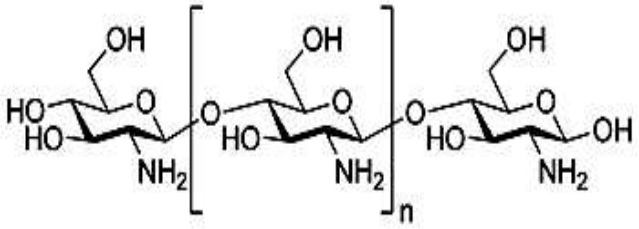

Figure:1 Chitosan-

* Assistant Professor, Chemical Engineering Department , MUET Jamshoro

** Civil Engineering Department, Universiti Teknologi PETRONAS, 31750 Tronoh, Perak, Malaysia

*** IARSCS/ HiTech RLs, University of Sindh, Jamshoro Pakistan

[1] Assistant Professor, Energy & Environment Engineering, QUEST, Nawabshah

2. PREPARATION OF CARBOXYMETHYL CHITOSAN:

Chitosan + Isopropanol (3gm/65ml) ⟹ NaOH + MCA* / Isopropanol 40% Sol (1:1m/m) ⟹ Carboxymethyl Chitosan

Chitosan−OH + **ClCH$_2$COOH** + **2NaOH** ⟶ **C**hitosan−O-**CH$_2$COONa**+ **NaCl**+ 2**H$_2$O**
(**C**hitosan) (MCA) (**SodiumHydroxide**) (**Carboxy**m**ethylC**hitosan)

*MCA = Monochloro acetic acid

3. RESULTS & DISCUSSION:

Organic modified material carboxymethyl chitosan when subjected to characterization proved satisfactory results. The techniques used for above studies were SEM, EDX & FTIR. The SEM with courtesy of Centre of Pure and Applied Geology University of Sindh Jamshoro, carried out on electron microscope model (JEOL 6490 LV – SEM by JAPAN).The prepared carboxymethyl chitosan showed crystal consisted of less than 10µm particle size. The scan prints suggest that it possessed crystalline surface. EDX studies were obtained byJSX-3400RII Energy-Dispersive X-ray model with Fluorescence Spectrometer detection system. .According to the results; the compound possesses 55.65%carbon, 34.36%oxygen, 5.30%nitrogen, 1.63% sodium and 1.91%chlorine. The compositions were determined from K shell under the particle size of 49.1nm- 62.5nm.

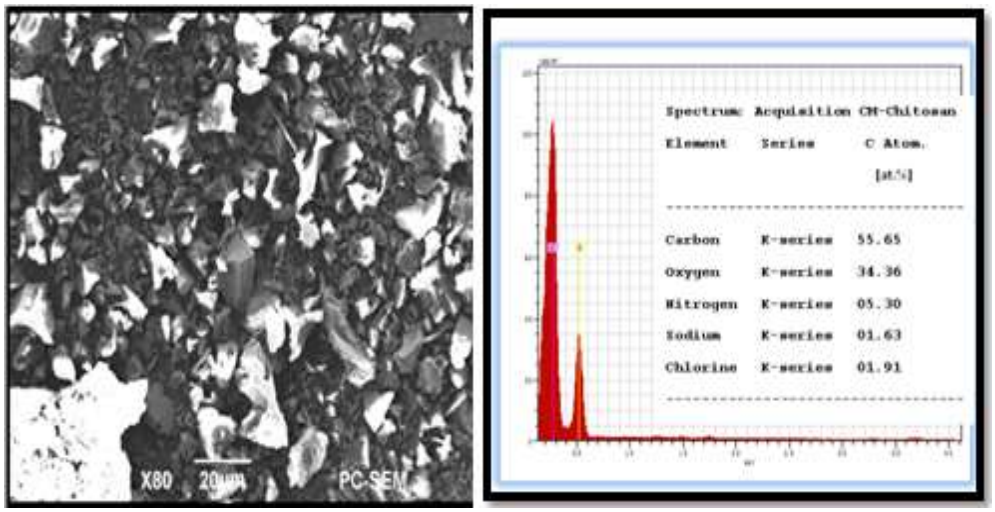

Figure.2: SEM &EDX Spectrumof Carboxymethyl Chitosan

Fourier transformation spectroscopy of carboxymethyl chitosan (fig.3), were conducted in Hitech Resources Laboratories, university of Sindh Jamshoro, Pakistan,byThermo Nicolet Avtar 330 FTIR (USA) with Zr-Se probe. Zeenat et al [7-9] reported FTIR of carboxymethyl chitosan having functional groups on skeleton. The band of spectrum at at 3436 cm^{-1}confirms stretching of O-H and N-H group. It further appears at 2900cm^{-1}due to stretching of C-H group. The band at 1634cm^{-1} appears due to asymmetrical stretching of C=O groups. Theband at 1420cm^{-1} suggests stretching of -CH_2 and -CH_3 groups.

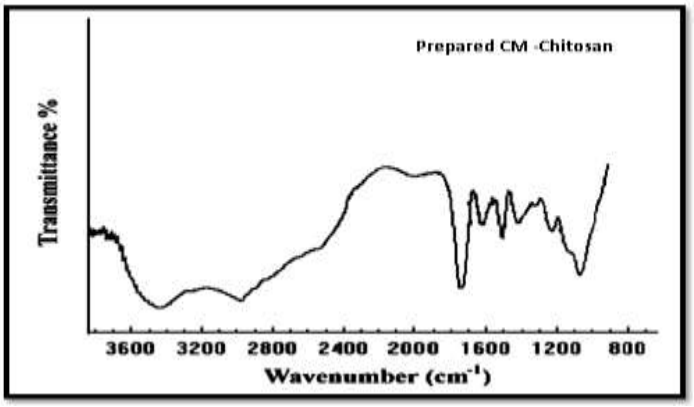

Figure 3: FTIR of Carboxymethyl Chitosan

4. METAL REMOVAL & RECOVERY BY COLUMN METHOD:

In present study five small columns were prepared each contained 2 gram carboxymethyl chitosan. The columns were eluted first with alkali solution of 10% NaOH. The columns were left for 2 hours then washed and neutralized at pH 7 with HCl diluted solution. The columns containing copper (lI), zinc (II),chromium (IIl), iron (II) and nickel (II) were examined for removal and recovery efficiencies from aqueous metal solutions with concentrations ranged from 10-100 mg/L. When compared the order of performance stood at Cu>Zn>Cr>Fe>Ni. On the contrary the ability of Cu(II) was foundbetter over other transition metals. During thiswork, the columns with 2 g carboxymethyl chitosan each for metals increased uptake capacity from 10-100 mg/L. Recovery of the metals was done with EDTA 84-100 % from industrial wastewaters (Table 2).

5. CALIBRATION CURVES OF METAL IONS BY ATOMIC ABSORPTION:

Calibration curves of metals were obtained using atomic absorption spectroscopy (AAS).The stock solution of 1000 mg/L of metals ions; iron, nickel, copper, chromium and zinc, were prepared from chloride salts of AR grade Merck (Germany). Appropriate dilutions were made for obtaining calibration curves [fig.4]. The above calibration curves of the metal ions were obtained by plotting absorbances on y-axis against concentration (µg/L) on x-axis [table.1].

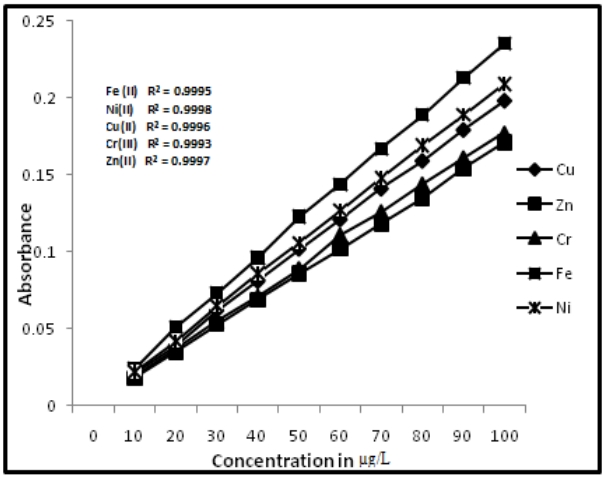

Figure 4: Calibration Curves of Metal ions by AAS

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TABLE1: Recovery and removal efficiencies of metals against standard metal solutions (mg/l)

Metal Concentration (mg/L)	Cu(II)	Zn(II)	Cr(III)	Fe(II)	Ni(II)
20	99.8 ± 0.4	99.2 ± 2.1	98.1 ± 3.6	99.7 ± 1.1	96.2 ± 3.8
40	99.7 ± 0.3	98.9 ± 3.5	97.8 ± 3.3	99.3 ± 1.4	96.1 ± 4.7
60	99. 5± 0.7	97.3 ±2.6	96.7 ± 2.8	98.7 ± 1.9	95.4 ± 4.6
80	99.1 ± 1.1	96.9 ± 3.2	96.3 ± 3.2	98.2 ± 2.3	94.7 ± 3.9
100	99.1 ± 2.4	95.2 ± 3.4	93.1 ± 3.8	97.6 ± 2.9	94.2 ± 4.5

METAL ION REMOVAL AND RECOVERY FROM WASTE WATERS

The metal ions removal efficiency of over 86.4% - 95.1% and recovery of 100% was observed for copper (132 mg/L), zinc (171 mg/L), chromium (118 mg/L), iron (353 mg/L) and nickel (96mg/L) from waste water collected from phuleli dumping site off Mirza Mohallah Hyderabad, Pakistan. The metal intake capacity of carboxymethyl chitosan from waste water was remarkable. During present work it was found that 1.0 g carboxymethyl chitosan could adsorb from 0.5 to 1.3 mg of metal ions [table.2]. The pH was not adjusted in performing this work

Table 2 : Recovery and Removal Efficiencies of Metal Ions from Waste Waters

Metal Concentration (mg/L)	Cu(II)	Zn(II)	Cr(III)	Fe(II)	Ni(II)
	132mg/L	*171mg/L*	*118mg/L*	*353mg/L*	*96mg/L*
Metal Removal Efficiency (%)	93.1 ± 0.5	94.7 ± 1.3	95.1 ± 0.6	94.1 ± 1.0	86.4 ± 1.3

CONCLUSION

A new method based on small columns have been developed containing 2 grams of carboxymethyl chitosan and applied for removal and recovery of metal ions (mg/L); copper 132, zinc 171, chromium 118, iron 353 and nickel 96 respectively.

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