Synthesizing and characterization of chitosan graft co polymer: adsorption studies for Cu (II) and Cr (VI)

Hemalatha. R¹, Chitra. R², Xavier Raja Rathinam³, Sudha. P N⁴
1 - Part - Time Research Scholar, Manonmanium Sundaranar University, Tirunelveli, Tamil Nadu, India
2 - Part - Time off Campus Scholar, Dravidian University, Kuppam, Andhra Pradesh, India
3 - Associate Professor, Sacred Heart College, Tirupattur, Tamil Nadu, India
4 - Department of Chemistry, DKM College for Women, Vellore, Tamil Nadu, India
parsu8@yahoo.com
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ABSTRACT

Chitosan – g – maleic anhydride (MA) was synthesized by reaction of chitosan with maleic anhydride in N, N-dimethyl formamide. Chitosan – g – maleic anhydride – g – (acrylonitrile) co-polymer was prepared via free radical polymerization using ceric ammonium nitrate as the initiator. The effect of polymerization variables including initiator concentration, monomer concentration and reaction temperature on grafting percentage were studied. It was found that the grafting yield and grafting efficiency were increased with increasing the polymerization and then decreased. The grafting was maximum at 1.4 g of initiator (CAN), 2 g of the monomer (acrylonitrile) at 70 °C. The co polymer obtained was confirmed by FTIR, XRD, TGA and DSC analysis. This graft co polymer was used as an adsorbent in dye effluent treatment. Equilibrium sorption experiments were carried out. Data were tested with three isotherm models like Langmuir, Freundlich, and Dubinin – Radushkevich isotherm model. Their trends of applicability from the R² values follows the order Freundlich > Langmuir > D – R.

Keywords: Chitosan, graft copolymer, grafting percentage, adsorption isotherm, wastewater treatment.

1. Introduction

The continuously increasing demand for the commodities produces by chemical industries has triggered heavy metals accumulation in the eco system. Water is polluted in many ways like effluent of leather and chemical industries, electroplating industries and dye industries (Sudha, 2010). Contamination of aquatic media by heavy metals is a serious environmental problem (Baraka et al., 2007; Bose et al., 2002). Heavy metals are highly toxic even at low concentrations and can accumulate in living organisms, causing several disorders and diseases (Crini, 2006; Aksu, 2005; Forgacs et al., 2004). Metals can be distinguished from other toxic pollutants, since they undergo chemical transformations, are non – biodegradable, and have great environmental, economic and public health impacts (Kozlowski and Walkowiak, 2002; Rio and Delebarre, 2003). Several methods are used for the removal of heavy metals from aqueous solution such as, chemical precipitation, oxidation/ reduction, filtration, ion exchange, membrane separation and adsorption (Mohan and Pittman, 2006). Adsorption is the most frequently applied technique owing to its advantage such as variety of adsorbent materials and high efficiency at a relatively low cost (Babel et al., 2003; Wan Ngah et al., 2002). Although activated carbon is one of the most popular adsorbents for removal of metal ions (Mohan and Pittman, 2006; Nomanbhay and Palanisami, 2005; Babel et al., 2003).
Current investigations tend towards achieving high removal efficiencies with much cheaper non-conventional materials which are mostly cheap and abundant biological matter (Babel et al., 2003; Ansar Ali et al., 2011).

Recently, the removal of metals, compounds and particulates from solution by biological material is recognized as an extension to adsorption and is named as biosorption (Boddu et al., 2003). Many biosorbents such as fungi (Acosta et al., 2004), Algae (Gupta et al., 2001), seaweeds (Kratochvil et al., 1998; Elangovan et al., 2008) microorganisms (Sahin and Ozturk, 2005; Fan et al., 2008) and several biopolymers (Wu et al., 2008; Bailey et al., 1999). Chitosan is a biopolymer prepared through the deacetylation of chitin, which is the major component of crustaceans shells and the second most abundant biopolymer in nature has been widely used for the adsorption of heavy metal ions (Chu and Hashim, 2002; Guibal, 2004; Ravikumar, 2000; Onsøyen and Skaugrud, 1990).

Chitin is a white, hard, inelastic nitrogenous polysaccharide (Ravikumar, 2000). It is one of the principal ingredients of the carapaces, crusts and shells of crustacean. It is the second most abundant organic resource next to cellulose on earth (Muzzarelli, 1973). Only limited attention has been paid to chitin. Despite of its huge annual production and easy accessibility, chitin still remains an unutilized biomass resource primarily because of its intractable bulk structure (Kurita, 2001). Chitin because of its insolubility is rarely subjected to chemical reactions except for the preparation of chitosan by deacetylation. The structure of chitosan was shown in Figure 2. Khor has stated that 21st century can be the century of chitin taking a place as an extra ordinary material because chitin and its derivatives have exhibited high potential in a wide variety of fields (Medical, pharmaceutical, cosmetics, food industry, agriculture, environmental protection) (Khor, 2002; VanLuyen and Huong, 1996; Kas, 1997; Kurita et al., 1998; Peter, 2002; Hirano, 1999; Ravikumar, 2000).

Chitosan can be dissolved in only acidic solutions through the interaction between $H^+$ and $-\text{NH}_2$, but it is insoluble under higher pH conditions. It is also of limited solubility in organic solvents. In order to sort the above problems, chemical modification affords a wide range of novel chitosan derivatives. Among the various methods of modification graft copolymerization is an attractive technique to modify the chemical and physical properties of chitosan (Crini, 2005).

Grafting of chitosan allows the formation of functional derivatives by covalent binding of a molecule, the graft, on to the chitosan backbone. Chitosan has two types of reactive groups such as free amino groups and hydroxyl groups that can be grafted (Alves and Mano, 2008).

Two major types of grafting may be considered:

(i) Grafting with single monomer.

(ii) Grafting with two monomers.

The first type usually occurs in a single step, and the second may occur with either the simultaneous (or) sequential use of the monomers (Bhattachariya and Misra, 2004).

In the present study, we have synthesized graft co-polymer chitosan - g - maleic anhydride - g-(acrylonitrile) using ceric ammonium nitrate as the initiator. The prepared graft co-polymer was subjected to various analytical techniques such as FTIR, XRD, TGA, and DSC to confirm the grafting. Also we investigated the polymerization variables such as initiator concentration, monomer concentration and reaction temperature. This graft co-polymer will be highly useful for various application fields including drug delivery and wastewater
treatment. In present work efficacy of chitosan – g – maleic anhydride – g – (acrylonitrile) for treating dye industry effluent was attempted and found successful.

2. Materials and Method

2.1. Materials

Chitosan was purchased from India Sea Foods Cochin, Kerala, India. Maleic anhydride and Arylonitrile were of analytical grade and obtained from the company, Merck. All other chemicals were of analytical grade and used without any purification.

2.2. Preparation of chitosan – g – MA – g - (acrylonitrile) co polymer

2.2.1. Preparation of N- maleilated chitosan

Chitosan (2 g) and maleic anhydride (6 g) were dissolved in 100 ml of dimethyl formamide (DMF), and then the mixture was stirred at 130 °C for 3hrs under nitrogen atmosphere. The resultant solution was cooled to room temperature and poured in to ice water to precipitate the product. The product was collected by filtration, washed with diethyl ether for three times and then dried in vaccum at 40 °C. The grayish white powder of N-maleilated chitosan was obtained (Jinchen Fan et al., 2009).

2.2.2. Preparation of chitosan – g - MA – g – (acrylonitrile)

The graft co- polymer was homogeneously synthesized in aqueous solution by using ceric ammonium nitrate as an initiator. A mixture of 0.5 g of maleilated chitosan and 1.4 g CAN/10ml of HNO₃ was stirred followed by the addition of acrylonitrile (2 g). The reaction was performed at 70 °C for 1hr. The contents of the flask were cooled to room temperature and poured into 10%NaOH solution to precipitate the graft co-polymer.

The effect of initiator concentration, monomer concentration and reaction temperature on the grafting yield and grafting efficiency were investigated. The grafting efficiency (GE %) and grafting yield (G %) were calculated as follows,

\[ GE\% = \frac{W_g}{W_g + W_i} \times 100 \]  
(1)

\[ GY\% = \frac{W_g - W_i}{W_i} \times 100 \]  
(2)

\[ G\% = \frac{W_g}{W_a} \times 100 \]  
(3)

Where,

\( W_a \) = Weight of Acrylonitrile.

\( W_i \) = Weight of chitosan - g - MA.

\( W_g \) = Weight of chitosan – g - MA –g – (Acrylonitrile).

The possible reaction mechanism of chitosan with maleic anhydride and acrylonitrile was shown in Figure.1.
Figure 1: Scheme of possible mechanism

Figure 2: Structure of chitosan.
2.3. Characterization

2.3.1. FTIR

FTIR spectra of the grafted co-polymer products were determined by Perkin Elmer spectrophotometer and in a wide range wavelength between 400 cm\(^{-1}\) and 4000 cm\(^{-1}\) and in solid state using KBr pelletisation.

2.3.2. X – Ray Diffraction

X – Ray diffraction were obtained with a Dmax - 2200 X-ray diffractometer using graphite - monochromatized Cu K\(\alpha\) radiation (K = 1.54178Å\(^0\)).

2.3.3. Thermo gravimetric analysis

The thermal properties of samples were measured by NET Z SCH - Geratebau GmbH thermal analyzer. Samples were dried in vacuum desiccator and powdered in a standard Aluminium panel. 2.0mg of this sample was heated about 30 °C – 350 °C at a heating rate of 10 °C per min under N\(_2\) atm in the DSC analysis.TGA were recorded with 2.0mg of this sample was heated from 30 °C to 870\(^0\)C at a heating rate of 10 °C/min at N\(_2\) atm.

2.3.4. Dyeing industry effluent

Dyeing industry effluent was collected from an effluent canal outside a leather dyeing unit of Ranipet Industrial area, India in a polythene container. pH and Temperature were noted on the spot.

2.3.5. Physico-chemical characterization of effluents

Physico-chemical factors such as pH, Electrical Conductivity, Dissolved Oxygen, Biochemical Oxygen Demand, Chemical Oxygen Demand, Total Dissolved Solids, Total Solids, Alkalinity, Chloride, Hardness, Sodium and Heavy Metals such as Copper, Cobalt, Chromium and Zinc were analyzed as per the methods of APHA(1998), Heavy metals were analyzed using Varian AA200 Atomic absorption spectrophotometer(AAS) in air-acetylene flame.

3. Results and Discussions

3.1. FTIR

FT-IR is a promising tool to identify unknown substances and to determine the amount of components in a given sample. This test was performed to get authenticated information about the vibrational origin of the amide, carbonyl and alcoholic groups of chitosan and graft copolymers. FTIR spectrum of pure chitosan is shown in Figure 3. It shows a broad peak at 3429 cm\(^{-1}\) due to -NH stretching and -OH stretching peak at 1640 cm\(^{-1}\) 1592 cm\(^{-1}\) due to Amide I and Amide II groups. Peak at 1087 cm\(^{-1}\) indicates C-O-stretching, 1485 cm-1 peak due to C-N stretching. FTIR of CS – g - MA shows in Figure 4. A strong peak at 1596 cm-1 indicating C=C bond. This confirmed the grafting of maleic anhydride group on to chitosan (Guo et al., 2004). The FTIR of CS – g – MA – g – (acrylonitrile) shown in Figure 5. A peak at 2920 cm\(^{-1}\) and 2400 cm\(^{-1}\) indicating the CH2 stretching and cyano group also shows a peak at 573 cm\(^{-1}\) indicates the aliphatic nitrile group. This confirms the grafting of acrylonitrile on to maleilated chitosan. Usually the peak is obtained approximately at 2240 – 2250 cm\(^{-1}\) (Yan
– ming Dong and Zhi–qiang Li, 1999). But in this FTIR the peak was shifted due to double grafting.

![Figure 3: FTIR of chitosan](image)

![Figure 4: FTIR of chitosan – g – MA.](image)

![Figure 5: FTIR of chitosan – g – MA – g – (acrylonitrile)](image)
3.2. XRD

The XRD spectrum of chitosan shown in Figure 6. It has low crystallinity and the characteristic peak at 20=10° and 20° are assigned to crystal forms I and II. In comparison with chitosan, chitosan-g – MA – g – (acrylonitrile) does not have the peak at 100, but chitosan – g – MA – g – (acrylonitrile) graft co polymer have the peak at 2θ=280 in Figure.7. The intensity of the peak descends sharply. Hence crystallinity of the grafted copolymer had decreased much.

![Figure 6: XRD of chitosan.](image)

![Figure 7: XRD of chitosan – g – MA – g – (acrylonitrile).](image)

3.3. TGA

The TGA thermo grams of chitosan, chitosan – g – MA and chitosan – g – MA – g – (acrylonitrile) graft co polymer are presented in Figures 8 – 10. Chitosan has two degradation
temperatures which the temperature lowers than 100 °C indicating the loss of water. The temperature above 100 °C indicates the decomposition of pyranose ring structure. The TGA of grafted copolymer shows five decomposition temperatures. Maximum decomposition was observed around from 270 °C, which may be due to the decomposition of side chains, which was grafted on to the chitosan backbone

![Figure 8: TGA of chitosan.](image)

![Figure 9: TGA of chitosan – g – MA.](image)

![Figure 10: TGA of chitosan – g – MA – g – (acrylonitrile).](image)
3.4. DSC

DSC curves CS, CS – g - MA and CS - g - MA – g – (acrylonitrile) showed in Figures 11 – 13. Chitosan shows one endothermic and one exothermic peak. Endothermic peak can be attributed to the loss of water from chitosan. While the exothermic peak indicates the decomposition of pyranose structure. The chitosan – g – MA, chitosan – g – MA – (acrylonitrile) shows one endothermic, it indicates the evaporation of water, and exothermic corresponds to the decomposition of side chain. All the DSC curves showed the single Tg value which confirms the complete grafting of acrylonitrile on to the maleilated chitosan backbone.

![Figure 11: DSC of chitosan.](image1)

![Figure 12: DSC of chitosan – g – MA.](image2)
3.5. Effect of polymerization variables on grafting parameters of chitosan – g – MA – g – (acrylonitrile)

3.5.1. Initiator concentration

Figure 14 shows the effect of concentration of ceric ammonium nitrate (CAN) on the graft co-polymerization acrylonitrile on to maleilated chitosan by keeping other reaction variables constant. Both grafting percentage and grafting efficiency showed an increase at first, followed by a decrease with the increase of the initiator concentration. The increase of grafting percentage may be ascribed to the increase of macro radicals generated by the attack of more CAN for the saccharide unit of maleilated chitosan and therefore, the more active sites of maleilated chitosan reacting with acrylonitrile. When the concentration of CAN was further increased more than 1.4 g/10 ml HNO3, the concentration of radicals increased and consequently initiated more of the homopolymerization of a acrylonitrile, which resulted in the decrease of both GP% and GE%.

Figure 14: Effect of initiator on grafting.
3.5.2. Effect of Monomer concentration

The effect of monomer concentration on grafting parameters GE and GY are shown in Figure 15 which indicates an initial increase, followed by a decrease with the increase of monomer charged. The maximum is reached when the weight of acrylonitrile is 2 g. The increasing tendency is ascribed to the accumulation of monomer molecules in close proximity to the maleilated chitosan backbone due to the increase in monomer concentration. As the graft co-polymerization progresses due to the depletion of the available monomer, and reduction in the active sites on the backbone, results in a decrease in both GE and GY. The continuous decrease of GP with the increase of acrylonitrile concentration could be associated with the fact that more monomer molecules are helpful for homo polymerization than for graft co-polymerization.

![Figure 15: Effect of monomer on grafting.](image)

3.5.3. Effect of reaction temperature

The effect of reaction temperature (40 to 90 °C) on graft co-polymerization of acrylonitrile onto maleilated chitosan is shown in Figure 16 and investigated by changing the temperature from 40 to 90 °C, while keeping other reaction variables constant. It shows both GP and GE reached a maximum at 70 °C. When the reaction temperature was low the graft co-polymerization did not progress readily.

![Figure 16: Effect of temperature on grafting.](image)
Higher temperature was helpful in increasing the chance of collision for CAN on maleilated chitosan, which led to the increase of maleilated chitosan radicals and therefore enhanced the graft Copolymerization. On the other hand, GP and GE decreased with a further increase in temperature, probably due to the greater possibilities of termination and chain transfer at a relatively higher reaction temperature. The prepared graft co polymer chitosan – g – MA – g – (acrylonitrile) was investigated for the suitability for waste water.

3.6. Dye effluent treatment

The physico – chemical parameters and heavy metals content of the dyeing industry effluent collected from an industry from Ranipet industrial area. All the parameters along with the heavy metal contents were found to be high than the accepted limits.

3.6.1. Effect of adsorbent dose on the dye industry effluent

Table 1: Effect of adsorbent dose of chitosan – g – maleic anhydride – g – (acrylonitrile) on the physico-chemical factors and metals of the dyeing industry effluent.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effluent</th>
<th>Adsorbent dose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 g</td>
</tr>
<tr>
<td>EC dsm$^1$</td>
<td>14.5</td>
<td>9.6</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>6750</td>
<td>3135</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>1460</td>
<td>710</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1475</td>
<td>545</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4575</td>
<td>1910</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>745</td>
<td>310</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>740</td>
<td>316</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>1450</td>
<td>525</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>1100</td>
<td>540</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>650</td>
<td>325</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>420</td>
<td>127</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>76</td>
<td>21</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>270</td>
<td>101</td>
</tr>
</tbody>
</table>

Various dosages of the prepared chitosan -g -maleic anhydride - g – (acrylonitrile) have been used to treat dye effluent. Table 1 explains the parameters such as COD, TS, BOD, and ions such as chloride, sulphate and also heavy metals such as copper, chromium, cobalt and zinc have been decreased drastically with the increase in the adsorbent dosage. The purification of water has been found at minimum amount of sample required (5 mg/L). Hence 5 mg was found to be the optimum dosage of graft co-polymer in treating the effluent time (Singh et al., 2009).

3.6.2. Effect of contact time on dye industry effluent

Table 2: Effect of contact time of Chitosan –g- Maleic anhydride -g – (acrylonitrile) on the physico- Chemical factors and metals of the dyeing industry effluent.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effluent</th>
<th>Contact time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>60</td>
</tr>
<tr>
<td>EC dsm$^1$</td>
<td>14.5</td>
<td>8.1</td>
</tr>
</tbody>
</table>
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The Table 2 shows the effect of time on the treatment of dye effluent by the chitosan – g – maleic anhydride – g – (acrylonitrile). On increasing the time the initial dye concentration reduces. After the treatment for 5 hrs all parameters reduced to the maximum extent. Hence 5 hrs was found to be an optimum treatment time (Guinesi and Cavalheiro, 2006).

3.6.3. Effect of pH on dye industry effluent

Table 3: Effect of pH on the physico-chemical factors and metals of the dyeing industry effluent.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effluent</th>
<th>pH 5</th>
<th>pH 6</th>
<th>pH 7</th>
<th>pH 8</th>
<th>pH 9</th>
</tr>
</thead>
<tbody>
<tr>
<td>EC dsm⁻¹</td>
<td>14.5</td>
<td>8.8</td>
<td>2.6</td>
<td>3.7</td>
<td>4.1</td>
<td>5.3</td>
</tr>
<tr>
<td>TDS (mg/L)</td>
<td>6750</td>
<td>3170</td>
<td>225</td>
<td>1170</td>
<td>1295</td>
<td>2500</td>
</tr>
<tr>
<td>TSS (mg/L)</td>
<td>1460</td>
<td>440</td>
<td>65</td>
<td>178</td>
<td>301</td>
<td>460</td>
</tr>
<tr>
<td>BOD (mg/L)</td>
<td>1475</td>
<td>410</td>
<td>104</td>
<td>195</td>
<td>275</td>
<td>425</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>4575</td>
<td>1210</td>
<td>144</td>
<td>365</td>
<td>1010</td>
<td>1450</td>
</tr>
<tr>
<td>K (mg/L)</td>
<td>745</td>
<td>295</td>
<td>72</td>
<td>140</td>
<td>210</td>
<td>290</td>
</tr>
<tr>
<td>Ca (mg/L)</td>
<td>740</td>
<td>290</td>
<td>105</td>
<td>165</td>
<td>225</td>
<td>370</td>
</tr>
<tr>
<td>Na (mg/L)</td>
<td>1450</td>
<td>310</td>
<td>75</td>
<td>105</td>
<td>165</td>
<td>320</td>
</tr>
<tr>
<td>Mg (mg/L)</td>
<td>1100</td>
<td>510</td>
<td>110</td>
<td>325</td>
<td>440</td>
<td>590</td>
</tr>
<tr>
<td>Zn (mg/L)</td>
<td>650</td>
<td>110</td>
<td>45</td>
<td>95</td>
<td>116</td>
<td>145</td>
</tr>
<tr>
<td>Cu (mg/L)</td>
<td>420</td>
<td>110</td>
<td>40</td>
<td>97</td>
<td>114</td>
<td>196</td>
</tr>
<tr>
<td>Co (mg/L)</td>
<td>76</td>
<td>28</td>
<td>7.0</td>
<td>12</td>
<td>28</td>
<td>42</td>
</tr>
<tr>
<td>Cr (mg/L)</td>
<td>270</td>
<td>150</td>
<td>15</td>
<td>75</td>
<td>110</td>
<td>135</td>
</tr>
</tbody>
</table>

The effect of pH on dye effluent treatment was studied. The reduction of all the parameters in the effluent by the grafted co polymer was found to be pH dependant. Table 3 showed that the there was maximum adsorption of all the parameters in the effluent by chitosan – g - maleic anhydride - g – (acrylonitrile) at pH 6.

3.7. Sorption isotherms

When any sorption system reaches a state of equilibrium, there is a defined distribution of sorbate molecules at the solid – liquid interface and also in the bulk at a particular temperature. This provides an idea of the capacity of the sorbent for the sorbate. The
maximum possible accumulation of the sorbate at the solid surface is a function of its concentration at a constant temperature and it can be expressed by the following relationship,

\[ q_e = F(C_e) \]  \hspace{1cm} (4)

Where, \( q_e \) is the amount of sorbate sorbed at equilibrium (mg/g), \( C_e \) is the equilibrium concentration of the sorbate (mg/L). \( F \) can be equated to the phrase “is a function of”. The mathematical modeling of sorption is a very powerful tool for understanding the sorption process and essential for process design and optimization (Esposito et al., 2002). Several equilibrium – based models have been used to describe the metal transfer between the solution and solid phase during the sorption process (Vijayaraghavan and Yun, 2006a).

### 3.7.1. Langmuir sorption isotherm

The Langmuir model, which is one of the most widely used, was initially proposed for the adsorption of a gas on the the surface of a solid, nevertheless it has been extended to include the sorption of solid at a solid – liquid interface. The Langmuir model suggests that the sorption occurs on the surface of the solid that is made up of elementary sites, each of which can adsorb one sorbate molecule, i.e. Monolayer sorption. It was also assumed that every sorption site is equivalent and the ability of sorbate to get bound there is independent of whether (or) not the neighbouring sites are occupied (Langmuir, 1918).

The Langmuir model is given as follows,

\[ Q_e = \frac{Q_0 b C_e}{1 + b C_e} \]  \hspace{1cm} (5)

The linearised form is,

\[ \frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \]  \hspace{1cm} (6)

Where, \( q_e \) (mg/g) and \( C_e \) (mg/L) are the sorbed metal ion on the sorbent and the metal ion concentration in the solution at equilibrium \( b \) (L/mg) is the constant related to the affinity of binding sites. \( Q_0 \) (mg/g) is known as the Langmuir constant, which represents the monolayer sorption capacity. Figures 17 and 18 explained the linearization of Langmuir model. In general for good sorbents, high values of \( Q_0 \) and low values of \( b \) are required (Kratochvil and Volesky, 1998). The calculated values are reported in the Table 6.

![Figure 17: Langmuir isotherm for copper](image-url)
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Figure 18: Langmuir isotherm for chromium

The affinity between adsorbate and adsorbent can be predicted using the Langmuir parameter to form the dimensionless separation factor $R_L$

$$R_L = \frac{1}{1 + bC_0}$$  \hspace{1cm} (7)

Where $C_0$ is the initial metal ion concentration and $b$ is the Langmuir isotherm constant, the adsorption process as a function of $R_L$. Tables 4 and 5 show the $R_L$ values for copper and chromium.

Table 4: $R_L$ values for copper.

<table>
<thead>
<tr>
<th>Initial concentration of Cu(II) in (mg/l)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.5392</td>
</tr>
<tr>
<td>100</td>
<td>0.7006</td>
</tr>
<tr>
<td>40</td>
<td>0.8540</td>
</tr>
<tr>
<td>20</td>
<td>0.9212</td>
</tr>
<tr>
<td>10</td>
<td>0.9590</td>
</tr>
</tbody>
</table>

Table 5: $R_L$ values for chromium.

<table>
<thead>
<tr>
<th>Initial concentration of Cr(VI) in (mg/l)</th>
<th>$R_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>0.4828</td>
</tr>
<tr>
<td>100</td>
<td>0.6512</td>
</tr>
<tr>
<td>40</td>
<td>0.8235</td>
</tr>
<tr>
<td>20</td>
<td>0.9032</td>
</tr>
<tr>
<td>10</td>
<td>0.9491</td>
</tr>
</tbody>
</table>

$RL > 1$ unfavorable, $RL = 1$ linear, $0 < RL < 1$ favorable, $RL = 0$ Irreversible (Hubbe et al., 2011).

3.7.2. Freundlich sorption isotherm
The Freundlich isotherm model, which is also very widely used. The Freundlich model proposes a monolayer sorption with a heterogeneous energetic distribution of active sites, and/ or interactions between sorbed species (Freundlich, 1907).

The Freundlich model can be expressed by,

\[ Qe = K_F C_e^{1/n}. \]  
\[ \log qe = \log K_F + \frac{1}{n} \log C_e. \]

where, \( K_F \) and \( n \) represent the Freundlich constants. \( K_F \) is indicative of the relative sorption capacity, where \( n \) is the measure of the nature and strength of the sorption process and the distribution of active sites. Figures 19 and 20 correspond the Freundlich isotherm of copper and chromium. Using mathematical calculation that \( n \) values between 1 and 10 represent beneficial sorption (Febrianto et al., 2009). Freundlich constants are represented in the Table 6.

![Figure 19: Freundlich isotherm for copper.](image)

![Figure 20: Freundlich isotherm for chromium.](image)
Table 6: Langmuir and Freundlich constants

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Langmuir constants</th>
<th>Freundlich constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_m (mg/g)</td>
<td>b (l/mg)</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>312</td>
<td>.004272</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>168</td>
<td>0.005356</td>
</tr>
</tbody>
</table>

According to the regression coefficients proved that the correlation of Freundlich model was strong with respect to the Langmuir model.

3.7.3. Dubinin – Radushkevich sorption isotherm

Dubinin – Radushkevich model (Dubinin and Radushkevich, 1947) is postulated within a sorption space close to the sorbent surface to evaluate the sorption free energy and to help to determine the nature of bonding either physisorption (or) chemisorptions. The D – R model can be expressed,

\[ q_e = q_m \exp (-k \varepsilon^2) \]  
\[ \ln q_e = \ln q_m - k \varepsilon^2 \]

where, \( q_m \) is the maximum adsorption capacity (mg/g), \( k \) is a constant related to the energy of adsorption and \( \varepsilon \) is the Polanyi potential which is calculated (Sarin and Pant, 2006; Ramnani and Sabharwal, 2006; Quintelas et al., 2008).

\[ \varepsilon = RT \ln (1 + 1/C_e) \]

\( R \) is the gas constant and \( T \) is the absolute temperature in Kelvin. The isotherm constants \( q_m \) and \( k \) were calculated from the slope and intercept of the plot of \( \ln q_e \) Vs \( \varepsilon^2 \). The mean free energy of adsorption (E) was calculated using the value of \( k \).

\[ E = (2k)^{0.5} \]
Figures 21 and 22 shows the D – R isotherm for copper and chromium. Accordingly, the value of E for copper and chromium are 0.3533 and 0.2529 kJ/mol respectively. The common regard about E is that it depicts adsorption by ion exchange, when its value is between 8 and 15 kJ/mol. The value of E calculated in this study is substantially lower than 8 kJ/mol, indicating that the adsorption of copper and chromium on chitosan graft co polymer occurs due to vanderwaals forces (Sari and Tuzen, 2008; Singh and Pant, 2004).

3.8. Sorption efficiency

The distribution coefficient of an adsorbent is defined as the ratio of the metal ion adsorbed to the amount in the liquid phase. Values of the distribution coefficient lower than 1.0 shows low sorption efficiency. In this study the values of distribution coefficient is higher than 1.0 as presented in Tables 7 and 8. The estimated values of the distribution coefficient indicated high efficiency of the chitosan graft co polymer for the treatment of wastewater containing Cu (II) and Cr (VI) ions (Bamgbose et al., 2010).

Table 7: Equilibrium sorption of copper and chromium on chitosan – g – MA – g – (acrylonitrile) at 25 °C pH 6

<table>
<thead>
<tr>
<th>Initial concentration of metal ions (mg/l)</th>
<th>Cu(II)</th>
<th>Cr(VI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>129</td>
<td>131</td>
</tr>
<tr>
<td>100</td>
<td>70</td>
<td>73</td>
</tr>
<tr>
<td>40</td>
<td>29</td>
<td>31</td>
</tr>
<tr>
<td>20</td>
<td>16</td>
<td>17.2</td>
</tr>
<tr>
<td>10</td>
<td>8.1</td>
<td>8.8</td>
</tr>
</tbody>
</table>
Table 8: Distribution coefficient of copper and chromium at 25 °C

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Equilibrium concentration of metal ion (mg/l)</th>
<th>Distribution coefficient Kd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>71 – 1.9</td>
<td>1.8169 – 4.2631</td>
</tr>
<tr>
<td>Cr(VI)</td>
<td>69 – 1.2</td>
<td>1.8985 – 7.3333</td>
</tr>
</tbody>
</table>

3.9. Thermodynamics

The thermodynamic property, Gibbs free energy was calculated by the following,

\[ \Delta G^0 = -2.303 \text{RT log } \frac{C_{ad}}{C_{eq}} \]  

(14)

The \( \Delta G^0 \) value of Cu (II) and Cr (VI) were -151.67 and -189.05, respectively. The negative value of Gibbs free energy indicates the spontaneous nature of adsorption process (Hamadi et al., 2001).

4. Conclusion

The graft co-polymer of chitosan – g – MA – g – (acrylonitrile) was synthesized through homogeneous graft co-polymerization of acrylonitrile on to N- maleilated chitosan in aqueous solution using ceric ammonium nitrate as initiator. The impact of polymerization variables including initiator concentration, monomer concentration and reaction temperature on grafting parameters were investigated.

FTIR, XRD, TGA and DSC analyses confirmed the introduction of the acrylonitrile side chain in to the N- maleilated chitosan backbone by graft co-polymerization. The effects of dosage, time and pH of the medium on adsorption efficiency of graft co-polymer were studied for wastewater dye effluent. According to regression coefficient the Freundlich adsorption isotherm was more fitted for copper and chromium than Langmuir, and also the value of E < 8, it indicates that the adsorption was physisorption. The adsorption distribution coefficient is greater than 1; it indicates that the adsorption of copper and chromium on to the chitosan – g – MA – g – (acrylonitrile) is more efficient. A significant result has been found for the industrial application. Hence the graft co polymer chitosan – g – MA – g – (acrylonitrile) can be used for waste water treatment at industrial level.

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5. References


