1. Introduction

Water is inevitable for activities starting from our day-to-day life uses to large scale industrial activities in factories. But a vast majority of the water resources are being polluted worldwide. It has been estimated that over 80% of the world’s wastewater is released into the environment, polluting the rivers, lakes and oceans [1].

At present, various technologies are available to eliminate heavy metals from the wastewater. Earlier investigators have used a wide range of technologies such as chemical precipitation, ion exchange, flotation, coagulation, adsorption and membrane filtration for heavy metal removal from contaminated waste water [2]. The chemical precipitation methods though effective, has a possibility of creating large rates of secondary pollution due to formation of large quantities of sludge and toxic fumes rather than being expensive [3]. Studies on the removal of Mn$^{2+}$ ions from synthetic wastewater by electrocoagulation process has revealed that the removal efficiency was independent of solution conductivity but is highly dependent on the initial concentration of contaminant [4]. However, electrochemical wastewater treatment technologies are associated with a relatively high capital investment and a costly power supply, so they are not widely used. Conventional membrane cleaning techniques can be very effective, but are economically...
not viable. Research studies indicate that, the adsorption process using activated carbon offers more flexibility in design and operation with ability to produce high-quality treated effluent but it is relatively expensive [5][6]. One of the other major problems with all of these processes is the selectivity of heavy metal removal, that is, even if a particular process is very effective for one metal ion, it is very inefficient for other ions.

The affordable nature of the membrane processes using the biopolymer compounds and carbon nanomaterials reported in the recent studies indicate its potential in addressing the global problem of wastewater treatment and environmental pollution. The removal of zinc and lead from aqueous dilute solutions by polymer enhanced ultrafiltration using unmodified starch as a new binding polymer has been studied [7]. The design and synthesis of a universal membrane for heavy metal removal by exploiting the high metal binding feature of the amyloid fibrils and high porosity of activated carbon has also been investigated [8].

In this paper on the development of a membrane using starch (containing amylose and amylopectin) as biopolymer and graphene oxide (GO) as carbon nanomaterial, we have focused on removal of heavy metals from effluent water with reliable and inexpensive technology. The major aims of the study include the synthesis of GO, characterization of the GO, composite preparation using starch- GO, development of the membrane, characterization and analysis of the heavy metal removal efficiency.

2. Methodology

Graphene oxide for the composite was synthesized by modified hummer’s method [9]. Rice starch had been chosen as the binding material for the membrane due to its cost effectiveness and easy availability. Five solutions were prepared by mixing 25 mg, 50 mg, 0.25 g, 0.5 g and 0.75g graphene oxide respectively in five beakers each containing 20 ml rice starch solution. These solutions were stirred thoroughly using magnetic stirrer for around 30 minutes to obtain rice starch-graphene oxide composite. Membrane was developed by dip coating method [10] [11] using cotton cloth as substrate (Figure 1). Synthetic heavy metal effluents of lead (Pb), cadmium (Cd), zinc (Zn) & magnesium (Mg) of different concentrations were prepared and was standardized in laboratory. This was then filtered through the membrane using a funnel and sample bottle arrangement.

![Figure 1. Membranes developed using 0.25 g, 0.5 g & 0.75 g GO](image-url)
The prepared GO was characterized by Raman spectroscopy. The characterization of starch-GO composite was done by using SEM. The concentration of heavy metal atoms such as Pb, Cd, Zn and Mg in the initial and membrane filtered samples were determined using Atomic Absorption Spectroscopy (AAS). The obtained values were used to estimate the heavy metal removal efficiency of the membrane.

3. Results and discussion

3.1 Characterization of graphene oxide

Graphene oxide is produced from graphite, which is a cheaply available and most stable form of carbon [12]. Raman spectroscopy is a widely used tool for the carbon products due to presence of conjugated, C-C double bonds that can lead to high Raman intensities. For most carbon based materials, the main characteristics of the Raman spectra are the D band and the G band, which are assigned to the sp³ and sp² bonding states, respectively [13]. In the Raman spectrum of GO, the in-phase vibration (G band) is at 1567.04 nm and the disorder band (D band) is at 1339.2 nm [14]. The Raman spectrum obtained in our studies, shown in figure 2a also exhibited similar characteristics when compared with reference indicated in figure 2b.

![Raman spectrum of synthesized GO](image)

**Figure 2.** (a) Raman spectrum of synthesized GO (b) Reference Raman spectrum of GO [14]

3.2 Characterization of membrane

SEM is an excellent technique that can provide the detailed information on the morphology and structure of materials [15]. Therefore the characterization of the membrane was done by taking the SEM images of the starch-GO composite. The composites prepared using 20 ml rice starch & 0.5 g GO were observed using SEM to obtain the images as shown in figure 3. The fibrous metal binding sites formed between GO particles and the amylose/amylopectin in starch is clearly evident from these images.

![SEM images of rice starch- GO composite](image)

**Figure 3.** SEM images of rice starch- GO composite at different magnification
3.3 Analysis on the heavy metal removal efficiency of membrane
The AAS results of the effluent samples by varying certain parameters were consolidated and tabulated to analyse the heavy metal removal efficiency of the prepared membranes.

Approximately 100 ppm solution concentrations of heavy metal ions (Pb, Cd, Zn & Mg) were filtered through membranes, made out of composites prepared from varying amount of GO (25 mg, 50 mg, 0.25 g, 0.5 g, 0.75 g) in 20 ml rice starch and the results obtained has been tabulated in table 1. These results show that the removal efficiency of membrane had increased for all metal ions, with increasing amount of GO in the composite membrane as depicted in the figure 4. It is also noticed that 0.5g and 0.75g of GO concentration in rice starch- GO composite gave almost same removal efficiencies. So it can be presumed that the membrane prepared with 0.5g of GO has an optimum removal efficiency of 85-87% in the experimental conditions adopted.

Table 1. AAS results on varying the amount of GO in rice starch-graphene oxide composite

| Graphene Oxide (g) | 0.025 | 0.05 | 0.25 | 0.5  | 0.75 |
|-------------------|-------|------|------|------|------|
| Initial Conc.(ppm)| Pb    | 99.2 | 99.2 | 99.2 | 99.2 |
| Final Conc.(ppm)  | 80.35 | 64.48| 35.41| 14.89| 84.98|
| Removal Efficiency (%) | 19.00 | 35.00| 64.30| 84.98| 86.99|
| Initial Conc.(ppm)| Cd    | 99.9 | 99.9 | 99.9 | 99.9 |
| Final Conc.(ppm)  | 74.92 | 58.63| 31.96| 13.98| 86.00|
| Removal Efficiency (%) | 25.00 | 41.31| 68.00| 86.00| 87.60|
| Initial Conc.(ppm)| Zn    | 100  | 100  | 100  | 100  |
| Final Conc.(ppm)  | 85.04 | 70.02| 39.89| 21.02| 18.66|
| Removal Efficiency (%) | 14.96 | 29.98| 60.11| 78.98| 81.34|
| Initial Conc.(ppm)| Mg    | 98.99| 98.99| 98.99| 98.99|
| Final Conc.(ppm)  | 77.77 | 61.94| 36.65| 14.74| 13.83|
| Removal Efficiency (%) | 21.43 | 37.42| 62.97| 85.10| 86.02|

Figure 4. Variation in % removal on varying amount of GO
The effect of variations in initial heavy metal ion concentration on the removal efficiency of membrane was analysed by preparing 10, 50, 100, 200 ppm solutions of each heavy metal ion (Pb, Cd, Zn, and Mg). This was then filtered by passing through the membrane made of rice starch-GO (0.5 g) composite. The AAS results obtained were tabulated in table 2 and graphically represented in figure 5. From this data it is clearly evident that % removal efficiency is very high (90-95%), for all the four metal ions analyzed when the inlet concentration is in the range of 10 ppm. Whereas the % removal efficiency decreases to 74-84%, when the inlet concentrations of the heavy metal is in the range of 200 ppm. For the initial concentration range between 10 ppm – 50 ppm, though the % removal efficiency is above 85%, it shows a tendency of decreased effectiveness with increasing inlet concentration. From these results it can be assumed that this membrane is very much suitable for the effluents having comparatively lower inlet concentrations of heavy metals.

Table 2. AAS results on varying initial concentrations of different heavy metals

| Heavy Metals | Initial Conc. (ppm) | Final Conc. (ppm) | Removal Efficiency (%) |
|--------------|---------------------|-------------------|------------------------|
| Pb           | 10.0                | 0.809             | 91.91                  |
|              | 49.1                | 6.19              | 87.38                  |
|              | 99.2                | 14.89             | 84.98                  |
|              | 198.9               | 39.99             | 79.89                  |
| Cd           | 9.5                 | 0.502             | 94.72                  |
|              | 48.9                | 4.89              | 89.99                  |
|              | 99.9                | 13.98             | 86.00                  |
|              | 199                 | 37.77             | 81.02                  |
| Zn           | 9.7                 | 0.94              | 90.27                  |
|              | 49.7                | 7.52              | 84.87                  |
|              | 100                 | 21.02             | 78.98                  |
|              | 199.2               | 50.54             | 74.63                  |
| Mg           | 9.2                 | 0.697             | 92.42                  |
|              | 49.4                | 5.78              | 88.30                  |
|              | 98.99               | 14.74             | 85.10                  |
|              | 199.5               | 37.86             | 81.02                  |

For devising a more reliable waste water treatment model, the suitability of membrane in removing heavy metals in its combined state was also experimented. The analysis using combined heavy metal synthetic effluent is tabulated in table 3. It indicates that the % removal efficiency in the combined state (88-92%) is comparable to that of the individual heavy metal ion samples. Therefore this membrane prepared from 0.5g GO and rice starch can be highly effective in the removal of almost all heavy metal ions studied, with initial concentration ranging from 5 ppm to 15 ppm.
Figure 5. Effect of initial effluent concentration on % removal

Table 3. AAS results of combined synthetic heavy metal effluent

| Heavy metals | Initial Conc. (ppm) | Final Conc. (ppm) | Removal Efficiency (%) |
|--------------|---------------------|-------------------|------------------------|
| Pb           | 12.45               | 1.36              | 89.04                  |
| Cd           | 4.09                | 0.35              | 91.32                  |
| Zn           | 12.37               | 1.41              | 88.56                  |
| Mg           | 12.29               | 1.25              | 89.76                  |

4. Conclusion

The present work suggests that the starch-GO composite membrane is cost effective and highly suitable to be used for heavy metal removal from waste water. It is highly efficient for removal of heavy metals in lower concentration range (5ppm-15-ppm). The results obtained from this studies may be helpful for the future investigators for devising novel strategies for the treatment of waste water effluents from industries by conducting further experiments for optimization in this regard.

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