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CHITOSAN COATED SURFACE MODIFIED POLYPROPYLENE FABRIC FOR THE REMOVAL OF CD(II) AND ZN(II)IONS FROM AQUEOUS SOLUTION

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Abstract : Chitosan coated on a polypropylene fabric enhances the mechanical stability and reduces gel forming behavior of chitosan. Chitosan coated on H_2SO_4 treated polypropylene fabric and cross linked with glutaraldehyde was used for the preparation of filter. The quantity of the chitosan coated PP fabric was studied using thermo gravimetric analyzer. The Adsorption studies of Cd(II), Zn (II) ions was carried out in a batch process at room temperature in static manner with varying all possible parameters such as pH of solution, adsorbent concentration, metal concentration etc. Metal concentration was measured using ICP AES. It has been shown that CS coated PP fabric is an excellent adsorbent for heavy metals and a filtering unit may be fabricated using this technology at lower expenses.

Keywords : Chitosan, Surface modification, Polypropylene fabric, Heavy metal removal, Cross linking with glutaraldehyde

Abbreviations : PP- Polypropylene, CS-Chitosan, GA- Glutaraldehyde

I. INTRODUCTION

Pollution caused by heavy metals is a world wide phenomenon. Metals, which are significantly toxic to human beings and ecological environments, include cadmium (Cd), nickel (Ni), chromium (Cr), zinc (Zn), copper (Cu), lead(Pb), mercury (Hg) etc. They are important contaminants in the liquid and solid wastes of a number of industries such as paint, glass operations, dyes, batteries, electroplating, mining etc. The concentrations of some of the toxic metals from these industries are higher than permissible discharge levels. Heavy metals are very toxic because, as ions or in compound forms, they are soluble in water and may be readily absorbed into living organisms. After absorption, these metals can bind to vital cellular components, such as structural proteins, enzymes etc and interfere with their functioning. In humans, some of these metals, even in small amounts, can cause severe physiological and health effects [1]. It necessitates removing heavy metals from these wastewaters by an appropriate treatment before releasing them directly into the environment. Cd & Zn removal is well discussed in this work. Zn & Cd are softer, with lower melting and higher electro positive than their neighbouring transition group metals , the chemistry of cadmium is homologous to Zinc. *Cadmium* is an irritant to the respiratory tract and Prolonged exposure to this pollutant can cause emphysema, pneumonitis, proteinuria , osteomalacia, liver dysfunction , kidney damage manifested by anaemia & hyper tension. Zinc toxicity from excessive ingestion is uncommon but causes gastrointestinal distress and diarrhoea[2].

A wide range of physical and chemical processes are available for the removal of toxic metals from waste water. Conventional methods that have been used to remove heavy metal ions usually include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. This conventional method have several disadvantages like generation of sludge, high cost, partial removal of certain ions etc[3] Adsorption using activated carbon can remove heavy metals from waste water [4]. However, its wide spread use in waste water treatment is restricted due to its higher cost [5].

Biosorption method is one of the recent method widely used for heavy metal removal due to its profound availability and low cost. [6], [7]. It can be simply defined as removal of metals by any living organism by process of bioaccumulation. Algae, bacteria and fungi and yeasts have proved to be potential metal biosorbents. Biosorption, based on metal binding capacities of various biological materials and the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake is of great

concern. The major advantages of biosorption over conventional treatment methods are low cost, high efficiency, minimize chemical and biological sludge, reuse of biosorbent and possibility of metal recovery[8].
Chitosan has been investigated by several researchers as a biosorbent for the capture of heavy metals from aqueous solutions. Its use as a biosorbent is justified due to following significance (a) low cost compared to commercial activated carbon, (b) outstanding chelation behavior [9]. Chitin is a white, hard, inelastic, nitrogenous polysaccharide and is the second most abundant polymer in nature after cellulose. It can be extracted from shells of prawns, crabs, insects and other crustaceans [10]. Chitosan is the N-deacetylated derivative of chitin. A sharp nomenclature with respect to the degree of N-deacetylation has not been defined between chitin and chitosan . Chitin and chitosan are of commercial interest due to its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties, etc. [11]. Chitosan can be used as an adsorbent to remove heavy metals due to the presence of amino and hydroxyl groups, which can serve as the active sites. [12],[13]. However, chitosan is very sensitive to pH as it can either form gel or dissolve depending on the pH values [14].
Surface modification has become a popular method for providing a material with desirable properties for practical applications, and many methods of surface modification have been employed. Crosslinking with glutaraldehyde(GA) widely applied method of surface modification. It will stabilize chitosan in acid solutions and enhance its mechanical properties [15].It also increases its resistance to biochemical and microbial degradation. Moreover, chemical grafting of new functional sites improves extraction selectivity as well as maximum sorption capacities and pH sensitivity [16].
A proper and inexpensive material is used as immobilization support for chitosan to build the filter, can reduce the cost of the chitosan without effecting the metal adsorption capacity. The chitosan coated on a rigid material (glass beads, sand or filter fabric are desirable) enhances mechanical stability and reduces gel forming behavior and mass transfer [17]. The use of filter fabric is favored due to its large surface area, excellent control on flow transfer characteristics and the low cost, especially when nonwoven fabrics of Polypropylene (PP) is adopted. The appropriate surface modification of polypropylene can improve its properties like wettability, dyeability and adhesionproperties, which will increase the adhesion of chitosan coating [18].The detailed studies has been conducted by Jozef Ráhel' et. al and Maher Z. Elsabeea et. al on Plasma treatment of polypropylene fabric and chitosan coating [19],[20].
Not many investigations on chemical surface modification of PP has been reported."Surface Chemical Modification of Polypropylene Fiber Waste" was done in details by Jamerson et. al. The treatment of fabrics with concentrated H2SO4 revealed the presence of complex mechanisms involving sulfonation, oxidation, decomposition, and aromatization to form carbonaceous structures, A high concentration of cation exchange sites introduced on the PP fabric improve the wettability which may be used as a support for suitable adsorbing medium [21].The objective of the work is to develop a cost effective technology for the removal of heavy metals from industrial waste water. A detailed study of surface chemical modification of Polypropylene Fabric by H2SO4 was conducted and CS was coated on acid treated polypropylene fibre and cross linked with glutaraldehyde to improve the stability. Batch adsorption studies were carried out using the CS coated PP fibre to remove Cd(II) and Zn(II) ion from waste water

II. EXPERIMENTAL

A Reagents

Chitosan flakes with deacetylation degree of about 80% was collected from India Sea Foods, Cochin, India. Polypropylene nonwoven fabric purchased from local market was washed with distilled water, air dried and used. All other chemicals and reagents used in this work were analytical grade and used as received. The aqueous solution of metal ions was prepared from their acetate salt using Millipore water.

B Preparation of the filter

Surface modification of PP fabric: The Polypropylene nonwoven fabric was cut into square pieces of 15mm x15mm size. Each piece of dried fabric was weighed (Precisa balance with resolution of 0.01mg.) and treated with 100ml concentrated H_2SO_4 (98%, Merck) at 100^oC for 24 hrs. Then the fabric was extensively washed with distilled water and dried.
Coating of Chitosan: About 5g of chitosan was slowly added to 500 ml of 2.5% (v/v) acetic acid (99% , Merck) solution with constant stirring by a magnetic stirrer. Acid treated PP fabric was immersed in the acidic CS solution for 24hrs [22]. The CS Coated PP fabric was washed with distilled water and dried. The process (15 min of dipping) was repeated 3 times to form a thick coating [23]. The CS coated fabric was immersed in a coagulation bath made of 0.5% NaOH solution for 3hrs to neutralize the amino group.
Cross linking with glutaraldehyde : CS coating was heterogeneously cross linked with 0.75% (w/w) aqueous glutaraldehyde solution without agitation followed by rinsing with distilled water to remove unseated GA residue and weakly attached chitosan homopolymer. The newly formed filter was called GA crosslinked CS coated PP filter (GA-CS-PP Filter). The filters were dried and weighted prior to each adsorption experiment to get the average value of chitosan coating.

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C Characterization of CS coated PP filter

To determine the layers of Chitosan formed on the treated fabric, SEM (JEOL, JSM - 6390LV) micrographs for the GA-CS-PP Filter and acid treated fabric were taken. GA cross linked with Chitosan coating was confirmed with comparing FT IR spectrum (Thermo Nicolet, Avatar 370 with HATR Assembly) of the GA-CS-PP Filter and chitosan film. Chitosan coating on the treated fabric was confirmed by comparing FT IR Spectrum of Chitosan coated pp fabric and treated PP Fabric. The thermal properties of the CS coated PP fabric was studied using thermo gravimetric analyzer (Perkin Elmer, Diamond DT/TGA.).

D Batch adsorption studies

Batch adsorption studies were carried out using the GA-CS-PP Filter to remove Cd(II) and Zn(II) ion from waste water. Single metal ion experiments were performed with 10mg/L, 30 ml single metal ion solution in closed container using one piece of filter of about 0.3g weight. The magnetic stirrer was used to equilibrate the solution. The equilibration time was 24hrs. The filter was removed and filtrate was analyzed using ICP AES system (Thermo Electron, IRIS intrepid II).

Metal intake was computed by using the following expression

$$\text{Qe (mg/g)} = \frac{(Co - C1)}{m} V \qquad (1)$$

where Co and C1 are metal concentration before and after adsorption(mg/L),
V is the volume of adsorbent(L) and m is the weight of adsorbent(g).

$$\text{Percentage adsorption} = \frac{(Co - C1)}{Co} x100 \qquad (2)$$

The effect of pH of the solution on the adsorption capacity of GA-CS-PP filter was studied with varied pH range from 3.0 to 7.0 with metal ion concentrations of 10mg/L and 30 mg of filter. The pH of the solution was adjusted by using 0.1 M HCl or 0.1M NaOH solution. The effect of initial concentration and contact time study help to determine the capacity of filter to remove specific metal ions in the solution at equilibrium time.

The effect of initial metal ion concentration was studied by placing a filter in solution with varying metal ion concentration of 1, 3 and 10 mg/L and pH is adjusted to 7 for , Zn(II) and 6 for Cd(II) respectively. The suspensions were equilibrated by magnetic stirrer and kept for 24hrs. The effect of adsorption time was studied by varying time of contact of the filter with solution having a metal ion concentration of 10 mg/L and optimum pH. The suspensions were equilibrated by magnetic stirrer.

The effect of filtrate concentration was studied by varying the filter weight of 0.1, 0.2, 0.3, 0.4g & 0.6g respectively with solution having a metal ion concentration of 10 mg/L and optimum pH. The suspensions were equilibrated by magnetic stirrer.

III. RESULTS AND DISCUSSION

A Adsorbent characterization

The average mass difference of chitosan coated PP fabric and treated PP fabric was measured and was approximately 15 to 17% of the fabric weight.

SEM photographs of the treated PP fabric was used to observe the changes in the surface morphology. SEM images illustrate the modified surface of H2SO4 treated PP fiber (Fig.1. A & B). Figure shows the cavities formed on the PP fiber surface due to reaction with H2SO4. The GA-CS-PP Filter SEM image shows a thin uniform layer of chitosan formed on surface of treated PP fabric (Fig.1C).

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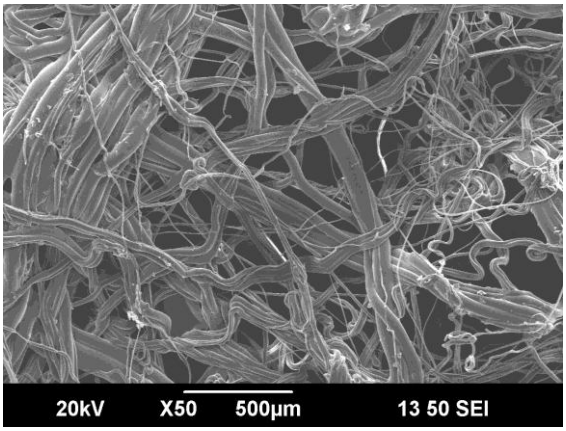

Fig.1.A

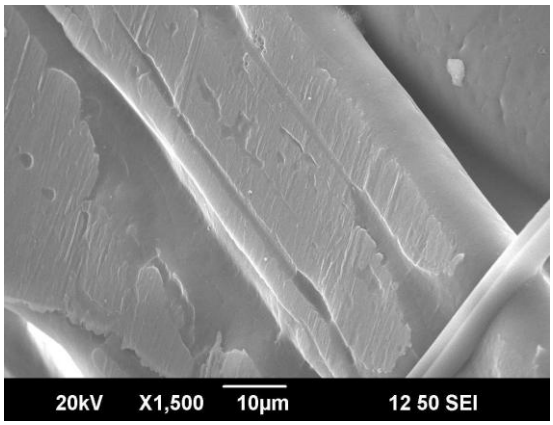

Fig.1.B

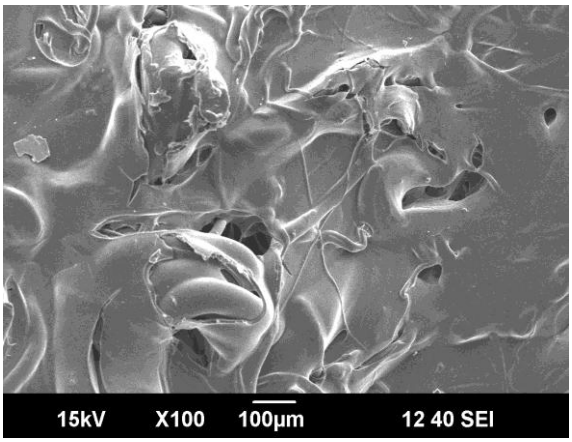

Fig.1.C

Fig.1. SEM Images, A. Polyproylene Fabric, B. Acid treated Fabric, C. Chitosan coated PP Fabric

The FTIR spectra of the glutaraldehyde cross linked Chitosan coated fabric(Fig.2 A) and acid treated fabric was taken (Fig.2.B). The vibration frequency of the chitosan layers showed at 3356 to 3533cm-1 which was due to the stretching vibration of the NH2 and the OH, and 1723 cm-1 and 1600 cm-1 which was due to the residual carbonyl groups. This spectrum indicates the presence of chitosan coating.

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Fig.2.A. FT IR Spectrum of GA-CS-PP Filter

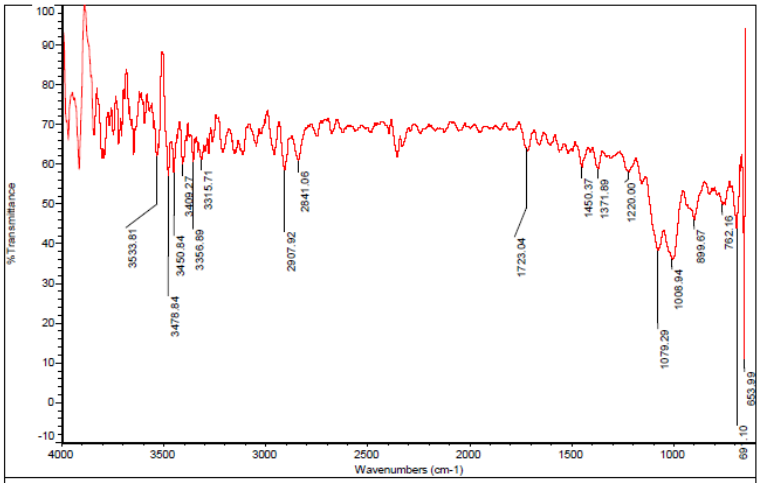
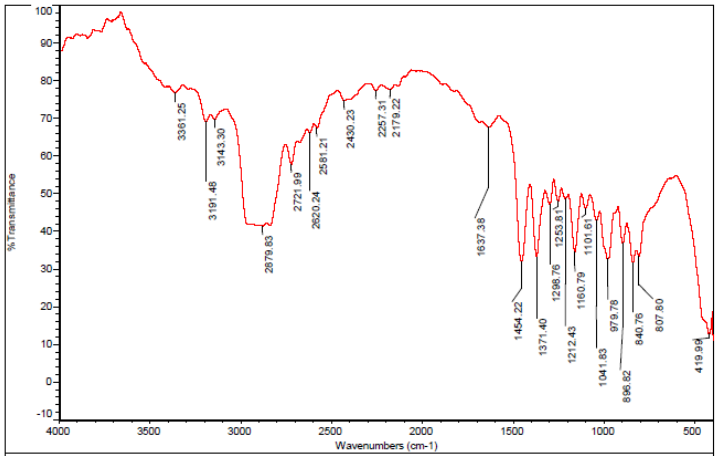


Fig.2.B FT IR Spectrum of Acid Treated PP Fabric



The Thermo gravimetric measurement of acid treated PP in nitrogen atmosphere shows a single weight loss at about 450oC related to the thermal decomposition of the polymer chain(Fig.3.A).TG graph of chitosan film(Fig.3.B) indicates water evaporation at 100^{o}C and predominant stage of thermal degradation appears at 275-300^{o}C caused by depolymerisation of chitosan chain (70% weight lose). TG graph of Chitosan coated PP filter (Fig.3. C) pointed out presence of chitosan as well as % of chitosan coated on the filter. The weight loss at 300^{o}C indicates the chitosan decomposition and about 16% drop in mass of the sample is observed at this point is the direct indication of 16% of chitosan samples burned out from film. This result indicates the chitosan coating on pp fabric was about 16% of the filter weight.

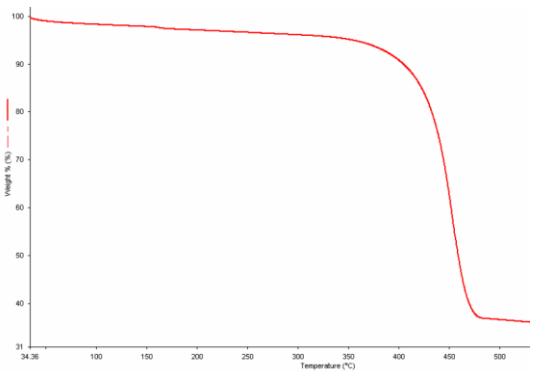


Fig.3.A

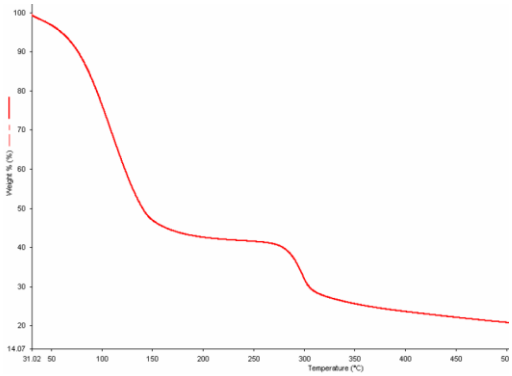


Fig.3.B

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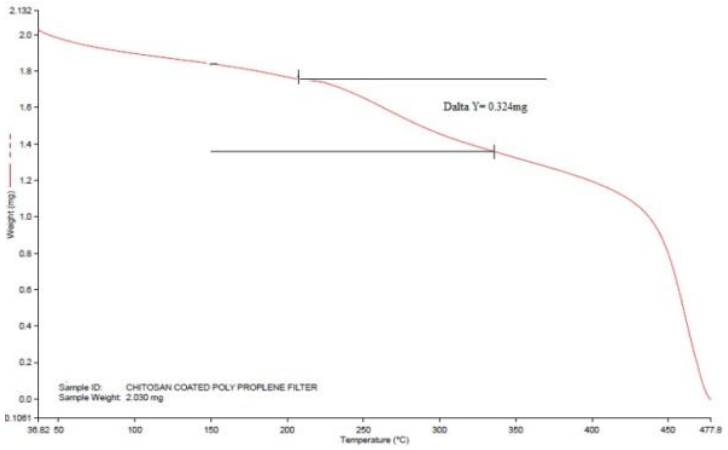

Fig.3.C

Fig. 3 Thermo gravimetric measurement of A. Acid treated PP , B. Chitosan film, C. Chitosan coated PP filter

B The effect of pH on adsorption of metal ions.

Experiments were conducted to determine the optimum pH for the Cd(II) and Zn(II) ion uptake by varying pH from 3 to 7, while keeping all other parameters constant. The graph (Fig.4) shows that the metal uptake by chitosan was pH dependent. The metal ion adsorption by the filter was found to be increased with the pH of the solution. Since the amino groups on the adsorbent surface get protonated at very low pH. The electrostatic interaction between the adsorbent surface and the metal ions to be adsorbed are electro statically repulsive [24]. However a favourable increase in adsorption as observed at higher pH, due to the formation of metal complexes. Maximum uptake pH for Zn(II) and Cd(II) are 7 and 6 respectively. It can be noted that metal ion uptake depends on the pH of the solution and GA-CS-PP filter can be effectively used for slight acidic and neutral solution

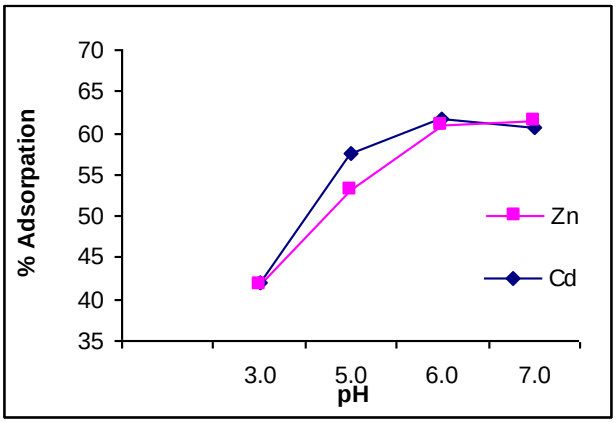

Fig.4. Effect of pH on metal ion adsorption of filter

C Effect of Initial concentration and contact time

The effect of initial metal ion concentration of 1 mg/L to 10mg/L on the adsorption of Cd(II) & Zn (II) into GC-CS-PP Filter was also examined. Table I list the percentage removal and absorption capacity at different initial concentration.

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Table I.
ADSORPTION STUDY OF GC-CS-PP FILTER

Cd(II) Concentration (mg/L)	% removel	Qe (mg/g)
0.71	98.88	0.08
3.81	89.51	0.43
10.22	61.82	0.95
Zn(II) Concentration (mg/L)	% removel	Qe (mg/g)
1.08	98.98	0.11
3.04	83.56	0.36
10.93	60.84	0.91

The Table-1 shows that increase in the initial concentration of Zn(II) and Cd(II) ion leads to increase in the adsorption capacity of GA-CS-PP filter as a function of contact times. The mass transfer effects and concentration gradient are directly proportional to the initial concentration
The fig.5 shows that adsorption equilibrium was gradually attained and major portion of the metal ion got adsorbed in the initial stage. Depending on the initial concentrations about 70–80% removal of metal ion was achieved during the first 4hrs of the contact time, The equilibrium time was about 6 hrs. The equilibrium adsorption capacity of Zn(II) and Cd(II) are 0.91 and 0.95 mg/g respectively. Cd(II) ions found to be more compared to Zn ions. This indicates the metal uptake of the filter, Qe may be based on ionic size [25]. Adsorption isotherm of the filter can be prepared using the data.

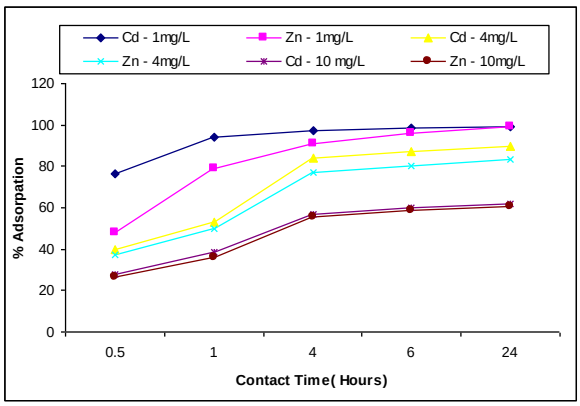

Fig.5. Effect of Initial concentration and contact time of Cd(II) & Zn(II) ions into Chitosan coated PP filter.

D The effect of adsorbent dosage
The adsorption has a great effect on adsorption process. The graph (Fig. 6) shows that the removal efficiency increased as the adsorbent dosage increased. Increasing the amount of adsorbent, will increases the availability of active sites of the adsorbent. Therefore, adsorption percentage and efficiency will also increases. The optimum value filter dosage for 10mg/L of ion solution was 0.3g for both Cd(II) & Zn (II) ions

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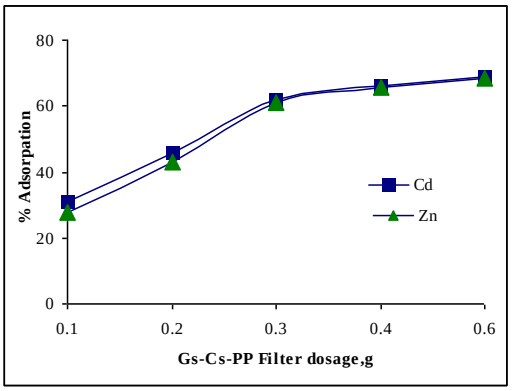

Fig.6 The effect of adsorbent dosage

IV. CONCLUSION

Chitosan was effectively coated on modified polypropylene fabric. About 16% by weight of chitosan was found coated on the PP fabric. The newly prepared biosorbent GA-CS-PP filter shows high efficiency in removing Zn(II) and Cd(II) ions from aqueous solution. The amount of metal ion uptake by the filter depends on the pH of the solution The equilibrium adsorption capacity of the adsorbent for Zn (II) and Cd (II) for 10mg/L solution are 0.91 and 0.95 mg/g respectively. In conclusion 'glutaraldehyde crosslinked chitosan coated polypropylene filter, (GA-CS-PP Filter)' can be packed in a waste water treatment column and it can be used as a cost-effective method for industrial effluent treatment.

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