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RESEARCH ARTICLE

COMPARATIVE STUDY OF ADSORPTION CAPACITY OF CHITOSAN HYDROGEL CROSSLINKED WITH FORMALDEHYDE AND GLUTERALDEHYDE AGAINST HEAVY METALS.

Varsha Bajpai[1], Manisha Prasad[1] and S.S. Narvi[2].

1. Department of Chemistry, SHIATS, Allahabad.
2. Department of Chemistry, MNNIT, Allahabad.

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Abstract

Chitin is a biopolymer, found in the crustacean. Chitin on deacetylation yield chitosan .In this study Chitosan hydrogel film used as adsorbent for removal of heavy metals. Chitosan hydrogel cross linked with formaldehyde and gluteraldehyde are used for removal of copper and nickel. FT-IR spectra show the attachment of new group in the chitosan hydrogel after cross linking. The swelling behavior of hydrogel ranges from 16% to 157% chitosan hydrogel, chitosan hydrogel cross-linked with formaldehyde shows swelling 21% 201% and chitosan hydrogel cross-linked with gluteraldehyde shows swelling 34% to 218%. The percentage removal of copper from both the cross-linked hydrogel is higher with respect to pH. Adsorption isotherm Langmuir and Freundlich is calculated with respect to contact time and pH.

Introduction:-

Water is essential necessity for human survival whose global demand doubles every after 21 years and its scarcity affects 40% of the world population (about 1.2 billion).It is projected to effect 2.7 billion people by 2025 the water borne diseases claiming annual death rate of 5 to 10 million. About 71% of the earth surface is occupied by water of which only about 0.05% is accessible for human consumption while the bulk of the remaining comprises of the inaccessible seawater, groundwater, swamps and frozen polar ice caps. The scarcity of water is due to rapid population growth, increased industrialization and decreased amounts of rainfall in the previous decades. Water pollution by heavy metal effluents released from industries has been identified as one of the consequences of worsening situation of water scarcity in the society **(Ngah *et al.*, 2010).** Increased environmental pollution as a result of industrialization is a major concern of the present world. Heavy metals are non-biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders **(Bailey *et al.*, 1999***)*.

A heavy metal is usually regarded as a metal having a relatively high density, atomic weight or atomic number, and is often assumed to be toxic. Some heavy metals, such as cadmium, mercury and lead, are highly toxic. Some of the commonly used heavy metal removal methods are coagulation, flocculation, membrane separation and adsorption. Adsorption techniques using chitosan composites have been developed to adsorb heavy metals as an alternative to conventional wastewater treatment processes (**Mouzdahir *et al.*, 2010).**

Corresponding Author:- Varsha Bajpai.
Address:- Department of Chemistry, SHIATS, Allahabad.

Chitosan is rarely found in nature but can be obtained from hydrolysis of chitin. Synthetically engineered chitosan copolymers represent a versatile biomaterial platform for wastewater treatment. Chitosan is shows Highly swelling behaviour, whose superabsorbent hydrogels are hydrophilic having three dimensional networks that can absorb water.

To improve the physiochemical properties of a chitosan matrix various functional groups may be introduce into a chitosan matrix after treatment with cross-linking agents.

In present study film of chitosan hydrogel and chitosan hydrogel crosslinked with formaldehyde and gluteraldehyde have been discussed. The spectroscopic characterized by (FT-IR). The swelling bevouir was observed with respect to pH and contact time. The removal of nickel and copper ion were observed on these film was calculated with respect to contact time and pH. Gluteraldehyde crosslinked chitosan hydrogel remove more metal from water than formaldehyde crosslinked hydrogel.

Experimental:-

Materials;-

Chitosan powder, glacial acetic acid, formaldehyde and gluteraldehyde.

Preparation of chitosan hydrogels:-

The preparation of hydrogels was carried out by cross-linking of the chitosan with formaldehyde and gluteraldehyde as per the method reported by (**Lin *et al.*, 2003),** in which 0.1 g chitosan was dissolved in 7 ml 1% glacial acetic acid solutions. After some hours, chitosan got converted into viscous transparent hydrogel, **Singh *et al.*, (2005).**

Crosslinking of hydrogel:-

After formation of hydrogel by dissolving it into 7ml of 1% glacial acetic acid, cross-linking was processed by adding varying amounts of (cross-linking agent) (formaldehyde/gluteraldehyde) into the hydrogel sample. Shown in table,

Sample no.	**Chitosan (gm)**	**Glacial acetic acid (ml)**	**Formaldehyde /glutereldehyde(ml)**
1	0.1	7	1.5
2	0.1	7	2.5
3	0.1	7	3.5
4	0.1	7	4.5
5	0.1	7	5.5

After the hydrogel was left for drying for 2 to 4 days, hydrogel film was formed.

FT-IR Spectral analysis:-

The Fourier transform infrared (FT–IR) transmission spectra were obtained from the film sample on a PerkinElmer Spectrum RX1 FT–IR spectrometer.

Swelling Measurements:-

After completion of cross linking reaction, weighed 0.1 gm chitosan hydrogel film was immersed in six solutions. Whose pH (1–6) and temperature (35°C) was maintained until they swelled to equilibrium. The pH values were precisely checked by a pH-meter (Digital pH meter IV) previously standardized with buffer solutions. The fully swollen samples were weighed after the removal of excessive surface water with filter paper. The swelling ratio can be calculated from the equation

Swelling ratio (%) = $[(W_s - W_d)/W_d] \times 100$:-

where W_s represents the weight in the equilibrium swollen state of the sample at experimental temperature and W_d, the weight of the dry state of the sample. **Singh *et al.*, (2005).**

Preparation of stock solutions of Metals (Copper & Nickel):-

- 0.5 gm $Cu(NO_3)_2$ dissolved in 1000 ml distilled water to prepare the Cu (II) ion solution. Initial pH of the solution was adjusted at pH 5. 0.5 ppm solution was formed.
- 0.5 gm $Ni(CH_3COO)_2$ dissolved in 1000 ml distilled water to prepare Ni (II) ion solution. The pH of the stock solution was adjusted at 5 pH, (**Singha *et al* ., 2013**)

Adsorption of Heavy Metals:-

Adsorption with Chitosan Formaldehyde cross-linked Hydrogel film:-

25 ml stock solution of Cu $(NO_3)_2$ was taken in 6 beakers and 0.1 gm chitosan formaldehyde cross-linked hydrogel was added to the solution in each beaker. The pH of the solution in different beakers was maintained from 1 to 6. The temperature of solution was adjusted at 35°C it was shaken and left for 4 hours. The initial concentration and final concentration was checked by using UV-spectrophotometer. Similar process was repeated for forming stock solution of Ni (II) ion and six samples of pH 1 to 6 were maintained.

Adsorption with Chitosan Gluteraldehyde cross-linked Hydrogel film:-

25 ml solution was taken from stock solution of Cu $(NO_3)_2$ in 6 beakers and 0.1 gm chitosan gluteraldehyde cross-linked hydrogel was added to the solution in each beaker. The pH of the solution in different beakers was maintained from 1 to 6. The temperature of solution was adjusted at 35°C it shaken and left for 4 hours. The initial concentration and final concentration were checked by using UV-spectrophotometer. Similar process was repeated for forming stock solution of Ni (II) ion and six samples of pH 1 to 6 were maintained (**Kanawade ., 2014).**

The formula for calculating the adsorption capacity of hydrogel is:

$$Q = (C_o - C_f)\ V/m$$

Where, Q = adsorption capacity, C_o= initial conc. of metal, C_f = final conc. of metal after absorption, V = volume of solution, m = mass of absorbent

Determination of Percentage Removal:-

Percentage removal, R (%) of metals from aqueous solution was calculated as

$$R\ (\%) = \{ (C_i - C_f)/ C_i\} \times 100$$

Where C_i and C_f are initial and final conc. of the metal in the solution respectively (**Talathoti et al., 2014).**

Adsorption Studies:-

The adsorption studies were performed by following Langmuir and Freundlich Adsorption Isotherms.

Results and Discussion:-

Chitosan is It is easily available and biodegradable and cheap adsorbent. The crosslinking Capacity, hydrophilic properties and water retention efficiency of hydrogel depends on the crosslinking agent. The polymers with hydroxyl group require drastic Conditions (low pH, high temperature, etc) in order to establish crosslinking with aldehydes whereas amine containing polymers can be crosslinked with the same reagent under mild conditions where Schiff bases are formed.

In this study the chitosan hydrogel was cross-linked by two cross-linking agents namely formaldehyde and gluteraldehyde. The cross-linking of hydrogels, stretching bond of present group in the hydrogel and attachment of new groups in the hydrogel was checked by using Fourier transform infrared (FT-IR) Transmission spectra and results were compared with chitosan.

Table 2:- Fourier Transform InfraRed (FT-IR) Transmission Spectra

Wavelength range $(cm)^{-1}$	Chitosan hydrogel	Chitosan formaldehyde cross-linked hydrogel	Chitosan gluteraldehyde cross-linked hydrogel	Assignment
3500-3000	3429	3428	3428	Bonded –OH groups
2999-2500	-	2930	2924	Alkane CH group
2499-2000	1656	-	-	-
1999-1500	-	1634	1640	Alkenyl C=C group
1499-1000	1027	1383,1119	1382, 1070,1227	C=O group
999-500	-	-	618	

In the FT-IR analysis peaks obtained show the attachment site of the metal atom. After cross-linking of hydrogel numbers of peak are increasing. It means the site of attachment of the metals atom increases .In the formaldehyde cross-linked hydrogel 5 peaks are present, while in the gluteraldehyde cross-linked hydrogel 7 peaks are present but in the chitosan hydrogel only 3 peaks are available. It shows that gluteraldehyde cross-linked hydrogel is better than formaldehyde cross-linked hydrogel and chitosan hydrogel. It has have more capacity to adsorb metals from water.

Effect of swelling:-

The swelling behaviour of chitosan cross-linked hydrogel was investigated at various pH (1, 2,3, 4, 5 and 6) and it was found is that water preservation efficiency of hydrogel is greatly affected by the amount of cross-linking agent. Swelling ratio of hydrogels increased till a certain point with increasing amount of cross-linking agent, but increased with excessive amount of crosslinking agent. Gluteraldehyde crosslinked chitosan hydrogel showed highest swelling ratio at 2nd sample (2.5 ml crosslinking agent used) while formaldehyde crosslinked chitosan hydrogel showed highest swelling ratio with 3rd sample (3.5ml crosslinking agent is used) shown in table 1. Gluteraldehyde showed better swelling ratio at low concentration.

Effect of pH on swelling in Chitosan Hydrogel:-

The pH of the solution affected the adsorption of water and swelling of chitosan hydrogel, 6 Samples were taken at 1-6 pH and room temperature. At pH6 chitosan hydrogel showed high swelling.

Effect of pH:-

The pH of the solution affected the adsorption of metals on both formaldehyde cross-linked chitosan hydrogel and gluteraldehyde cross-linked chitosan hydrogel. Initial and final conc. were investigated. Initially the adsorption was found low at lower pH and as the pH increased the adsorption also increased. The absorbance of UV radiations in both formaldehyde and gluteraldehyde cross-linked chitosan hydrogel has changed with the pH of the solution. The percentage removal of heavy metals has also changed accordingly. In this study maximum adsorption found at pH=6 in both the hydrogels.

Effect of contact time:-

The effect of contact time of effective removal of Cu^{2+} and Ni^{2+} ion from the water sample was investigated for 2 hrs, 4 hrs,6 hrs and 8 hrs, using constant concentration of metal ion**.**

Table 2:- Adsorption isotherm data for the removal of heavy metals with respect to pH.

Adsorbent	**Metal**	**Langmuir**			**Freundlich**		
		Q_{max} (mgg^{-1})	**R_L**	**R^2**	**K_f**	**Value of 'n'**	**R^2**
Chitosan hydrogel cross-linked with formaldehyde	**Cu^{2+}**	114	0.319	0.958	54.82	1.044	0.989
	Ni^{2+}	123	0.359	0.898	88.30	1.31	0.973
Chitosan hydrogel cross-linked with gluteraldehyde	**Cu^{2+}**	74.96	0.311	0.983	50.81	5.68	0.983
	Ni^{2+}	35.5	0.377	0.947	136.1	0.643	0.986

Based on the relationship of adsorption capacity for copper and nickel onto the adsorbents formaldehyde and gluteraldehyde crosslinked chitosan hydrogel and the equilibrium concentrations, the Freundlich adsorption isotherm have been correlated and the isotherm parameters are as presented in table 2. From the table it is clear that copper and nickel adsorption on the adsorbent have linear regression values ranging from 0.97-0.98. Similar results was obtained by **Elwakeel *et al.*, (2014**). In this study the value of n in case of formaldehyde crosslinked chitosan hydrogel for copper ion nickel ion are 1.044 and 1.31 respectively. The similar values for gluteraldehyde crosslinked chitosan hydrogel are 5.68 and 0.643.Out of these, only one value gluteraldehyde crosslinked chitosan hydrogel is 0.643. Therefore except this,other these cases are favourable adsorption of Freundlich isotherm model **(Ibrahim *et al.*, 2014)**

Table 3:- Langmuir and Freundlich isotherms- value of Cu^{2+} and Ni^{2+} with respect to Contact time.

Adsorbent	**Metal**	**Langmuir**			**Freundlich**		
		Q_{max} (mgg^{-1})	**R_L**	**R^2**	**K_f**	**Value of 'n'**	**R^2**
Chitosan hydrogel crosslinked with formaldehyde	**Cu^{2+}**	28.57	0.3192	0.918	926.8	0.295	0.98
	Ni^{2+}	27.04	0.3597	0.976	228.5	0.489	0.994
Chitosan hydrogel crosslinked with glutaraldehyde	**Cu^{2+}**	34.69	0.3111	0.957	557.1	0.346	0.989
	Ni^{2+}	44.59	0.3764	0.990	73.6	0.907	0.997

From the **table 3** the value of R_L is 0.3111 – 0.3764. and the value of R^2 is 0.918 0.990 for both adsorbent and heavy metals. The value is between $0 < R_L < 1$. It indicates that adsorption is favourable, similar result is obtained by **Ibrahim *et al*.,(2014**).

Conclusions:-

Chitosan derived from chitin ,it is biopolymer and easialy available in nature. The swelling retio is very high . It adsorbs water more than its weight. So it adsorb metals from water easily. It is low cost adsorbent . formaldehyde and glutereldehyde are cheap and easily available. Chitosan hydrogel eaisly crosslinks with formaldehyde and glutereldehyde. After crosslinking , the water adsorbing capacity increases. It does not require energy for the process. Further it is used for removaof heavy metals at low cost .

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