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Removal of Heavy Metals and Dyes from Wastewater using Hydrogels

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ABSTRACT

Hydrogels are 3D networks made up of synthetic or natural polymers which can hold large quantities of water hence are used in various fields. Since synthetic hydrogels water absorption capacity is high, and can be prepared by wide varieties of raw chemical resources and has long service life hence are replaced by synthetic polymers. Heavy metals and dyes are among the most toxic materials to the living areas, these compounds can be removed from the wastewater by the Adsorption process. Many methods have been used for removing different dyes and heavy metals. Various adsorbents have been used to remove different type of dyes and heavy metal ions from waste water such as, Lignocellulose waste, Activated carbon, and Clays. In this project hydrogels were used as a adsorbent to remove Heavy metal as well as dyes from wastewater, Chitosan is a type of polymer which is used here to prepare hydrogels. For obtaining the optimum conditions batch experiments were done by preparing synthetic water in the laboratory. effect of parameters such as, Agitation period, pH, initial concentration of dye and metals, Adsorbent dosage were also determined. For this parameters cross linked chitosan beads and CuO-Chitosan nano composites were found to be more efficient than that of non crosslinked beads, the crosslinked one's were more rigidity, and has resistance to acid medium. Adsorption behaviors were described by using Langmuir, Freundlich and Temkin Isotherm Models. Adsorption Data was well fitted to Langmuir Isotherm Models for both metals and dyes.

Keywords: Hydrogels(Chitosan), CuO-Chitosan nano composite, Adsorption, Dyes and Heavy Metals, Adsorption Isotherm, Adsorption kinetics.

1. INTRODUCTION

The potential sources of Dyes and Heavy metal ions from Industries such as textiles, leather, paper, plastics, metal fabrication, paints, batteries, fertilizers etc. Since many Heavy metals and dye compounds are harmful to human beings if discharged improperly to the environment .Adsorption is one of the efficient method to remove pollutants and impurities from wastewater. From literature studies chitosan have been identified as a good adsorbent. Chitosan is deacetylated form of chitin, which is a linear polymer of acetylamino-D-glucose. Recently chitosan that is used as an adsorbent because it have high contents of amino and hydroxy functional groups. In presence of this functional groups showing high potential of the adsorption of dyes and metal ions. some other useful features of chitosan includes its abundance, biocompatibility, non- toxicity, biodegradability, hydrophilicity and antibacterial property. Exclude/other than adsorption for removing dyes and heavy metals we have coagulation, flocculation, oxidation, membrane separation, ion exchange, precipitation methods. These methods are not widely used due to their high cost and economic disadvantage. In present adsorption techniques are the most versatile and widely used for treatment of wastewater. Some of the common adsorbents used are zeolites, activated carbon, alumina, silica gel etc. Here hydrogels (chitosan beads) are selected as an adsorbent material for removal of dyes and heavy metals and it showed good adsorption capacity on the Congo red dye and heavy metal ion like copper. these Hydrogels(beads) shows good efficiency at low pH but beads gets disintegrated in acidic medium to overcome this hydrogels have been cross linked with epichlorohydrin to stabilize the chitosan in acid solution. Cross linked chitosan is insoluble in acid solution of pH 1-7 and its mechanical properties are improved in presence of cross linker. Than hydrogels are incorporated with the Nano metal oxides (Copper Oxide) which showed better efficiency than the normal and ECH cross linked beads. To our knowledge the adsorption of dyes and heavy metals in the solution using chitosan beads was studied. In this work epichlorohydrin was selected as a cross linking agent and CuO was used to get better adsorption efficiency. The advantage of ECH is that it does not remove the cationic amine function of chitosan, which is the major adsorption site attracting the anion dyes during adsorption. The goal of this project is to study the adsorption behaviour of dyes and heavy metals using cross linked chitosan beads(both acidic and alkaline solutions) and CuO incorporated beads. We studied the adsorption isotherm and adsorption kinetics of Congo red dye and Cu ions on chitosan from the solution of different pH and other parameters. The Langmuir and Freundlich equations are used to fit the equilibrium isotherm. The adsorption rates were measured and determined quantitatively in correlation with initial dye concentration, pH, adsorbent dosage and agitation period. The obtained results will be useful for further application in dyes and heavy metals removal from wastewater.

2. LITERATURE REVIEW

It is important to remove dyes and heavy metals from the water because they contaminate the water as well as are harmful to the environment since the many Heavy metals and Dyes are highly toxic in nature. Therefore their concentration have to be reduced to levels such that its harmful effects have to be reduced before it enters into the environment, otherwise these can show some threats to the human as well as animal health. Heavy metals such as zinc, nickel, chromium, arsenic, copper, lead, cobalt, bismuth, ferrous and dyes from textile industry etc, Have been recognized as poisonous to the animals and Human beings even if they are present in traces. These are released from mining's, metallurgical metal finishing, battery manufacturing process, chemical manufacturing and some textile industries are leaving the toxic dyes in considerable amounts.

2.1. IMPORTANCE OF COPPER

Copper is used for various engineering purposes and it is one of the important material in the industry for making Alloys, also used in ceramic and pesticides. In many industries like automotive, electrical appliances, electronic, etc. copper is used in manufacture of wires. It is also used in algicides, copper forming industries. Wood preservatives and Copper compounds are used in fungicides. It is used in electroplating industry and manufacture of dye. Copper compounds are added to fertilizers and animal feed as a nutrient to support plant and animal growth.

2.2. EMISSIONS OF COPPER

Copper enter into the environment through natural and anthropogenic sources. Air and water is contaminated by copper from mining, milling, electroplating industries, petroleum and refining melting plant. Copper is discharge into the industrial effluents of various industries like chloral-alkali, electroplating, paints and dyes, petroleum refining, fertilizers, mining, and metallurgy, explosives, iron and steel industries etc. due to the direct discharge of industrial and municipal waste water is polluted. The main source of pollution in copper industries are: mine water and effluent from waste water treatment plants, sulphur containing gases, electrolyte from electro-refining plant.

2.3. ENVIRONMENTAL EFFECTS OF COPPER

Copper is regarded as one of the most toxic metal. The increase level of copper in environment is posing a serious threat to mankind. It can cause harmful biochemical effects, toxicity and hazardous disease in human beings.

Excessive intake of copper through air, water and food can cause harmful disease. Ingestion of 15-75 mg of copper can cause gastro-intestinal disorder. Excessive intake of copper can cause hepatoxic, hemolysis and nephro toxic effects. Copper toxicity can cause irritation, hepatic damage and central nervous system irritation followed by depression. Prescribed limit of copper in drinking water is 0.05mg/L as per WHO norms and also 0.05mg/L as per ISI prescribed limits.

2.4. CHITOSAN

Chitin is the 2nd most abundant natural polysaccharide next to cellulose. It was found in the shells of crustaceans such as crab, shrimp as well as in exoskeleton of marine zooplankton also have chitin in their wings. Chitin is found in the cell walls of yeast, mushrooms and fungi. Since the biodegradation of chitin is very dull in crustacean shell waste and accumulation of large quantities of discards from processing of crustacean due to this there is a major problem in the seafood industry so, recycling these by-products is very important. These by-products could used in various other industries for the treatment of wastewater. With help of these by-products many problems can be solved such as solid waste disposal effects. But chitin is an extremely insoluble material and it is a major problem that comforts the development of process and uses of chitin, and so far, very less large-scale industrial applications have been discovered. Chitin is one of the derivative of cellulose. Chitin is composed of a long chain of N-acetyl-D-glucosamine units. Professor C Rouget first discovered the chitosan in 1859. Chitosan is prepared by cooking chitin in alkali similar to the process for making soap. While preparing the glucosamine units are combining to form chitosan chains. Each glucosamine unit contains a free amino group. This amino group can take a positive charge which gives an amazing property to chitosan. A common method for the synthesis of chitosan is the de-acetylation of chitin using sodium hydroxide in excess as a reagent and water as solvent and this is used for commercial production.

Chitosan is soluble in acid solutions and is chemically more versatile than chitin or cellulose. In fact Chitosan is the only pseudo natural cationic polymer and this had been used in mini industrial applications for water treatment. Both Chitin and chitosan are widely used for wastewater treatment in many industries which leads to decreases the chemical oxygen demand and total nitrogen. Chitosan has limited applications of water treatment due to its low mechanical strength and flexible behaviour. On the other hand addition of synthetic polymers increases properties of chitosan. Chitosan also have disadvantages like acidic solubility, low thermal and mechanical stability. To overcome these draw backs chitosan can be modified physically as well as chemically.

3. METHOD

3.1. Chemicals

All the chemicals used were of analytical reagent grade. Chitosan (90% deacetylated, Indian marine sea foods limited) ,Congo red dye(Lab grade) and Copper sulphate pentahydrate were used without further purification. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout experimental studies. The structure of Congo red dye and chitosan is shown in figure1.

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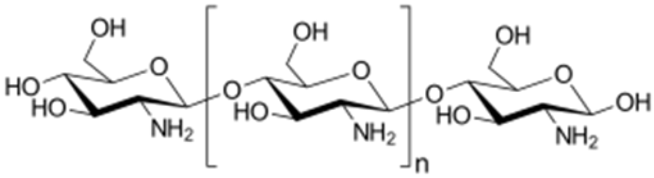

Figure1: Chitosan

3.2. Instruments

The list of the instruments used during the Adsorption experiments and there functions are given in table.

TABLE1: List of Instruments

Instruments	Function
Analytical balance	Weight Measurement
pH meter	Measurement of pH
Ultra pure water system	Preparation of stock solutions etc.
Photoelectric calorimeter 113	Estimation of metal ion and dye concentration
Shaker	Batch Adsorption studies
Magnetic stirrer	For Stirring

3.3. STOCK SOLUTION PREPARATION

3.3.1. Dye Solution Preparation

Stock solution of 50 ppm Congo red dye solution is prepared by dissolving Congo red dye(50mg) in distilled water contained in 1000ml volumetric flask. Hydrochloric acid and sodium hydroxide is used to adjust pH of solution.

3.3.2. Metal ion solution preparation

Stock solution is prepared by dissolving copper sulphate pentahydrate (39.28g) is added to distilled water contained in 1000 ml volumetric flask. HCL and NA0H were used to adjust pH of solution.

3.4. Preparation of Hydrogels(Chitosan beads) and ECH cross linking

Chitosan beads were prepared by dissolving 2g of chitosan powder in 60ml of 5% (v/v) Acetic acid solution in a beaker. The mixture was stirred by using magnetic stirrer for 20 min until gel formation. the formed gel is taken into the syringe and transferred into 0.5M sodium hydroxide solution. These beads were washed in distilled water to remove excess sodium hydroxide and stored in distilled water to prevent drying of beads.

Epichlorohydrin (ECH) is widely known cross linking agent. The wet non cross linked chitosan beads are weighed in a electronic balance, these beads are suspended in 1:2 (beads: ECH) ratio by weight of ECH. The beads in the

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ECH are agitated for a period of 3hrs at a temperature of 30 to 35 degree Celsius. The obtained are more rigid in nature and also have resistance to acid attack. The cross linked beads are washed in distilled water and stored in it till further use.

3.4.1. Preparation of Copper Oxide-chitosan nano composite

Copper oxide chitosan composite was prepared by dissolving 2g of chitosan in 60ml of 5%(v/v) acetic acid and stirred for 20 minutes, then 0.1 g of copper oxide nano powder was added to this viscous solution and stirred for 30 min. Then gel is taken into the syringe and transferred to the 0.5M sodium hydroxide solution keep it for some time and beads are washed with distilled water to remove excess sodium hydroxide and stored in distilled water for further use.

3.5. Experimental methodology

A known quantity of adsorbent is added to the dye and metal ion solution of known concentration ,then placed in flask shaker for specific time interval. Then adsorbent was removed, once adsorbent is removed the solution was analysed in Photoelectric calorimeter at the maximum wavelength for particular dye and metal ion solution. The absorbance values are noted at exact time, corresponding concentrations were determined from calibration chart.

3.6. Calibration chart

3.6.1. Calibration of Congo red dye

The Congo red dye sample is calibrated using absorbance values obtained for different concentrations. The calibration chart helps to identify respective colour removal capacity of adsorbent. The amount of dye adsorbed can be calculated using following equation.

$$q_t = \frac{V(C_o - C_t)}{m} \quad (1)$$

Dye removal efficiency can be calculated using following equation

$$R = \left(\frac{C_o - C_t}{C_o}\right) * 100 \quad (2)$$

Co is the initial dye concentration (mg/L), Ct is the concentration of dye at any time t (mg/L), m is the amount of adsorbent used (g), V is the volume of (L)

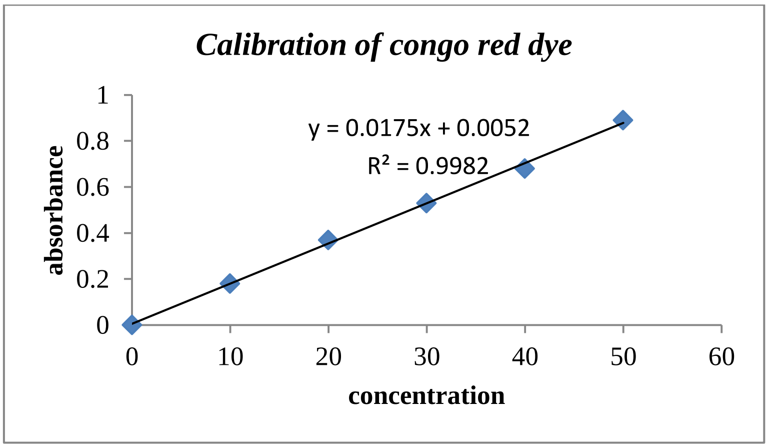

Figure 2: Calibration curve for Congo red dye

3.6.2. Calibration of Metal ions

The copper sulphate pentahydrate solution is calibrated using absorbance values for different concentrations.

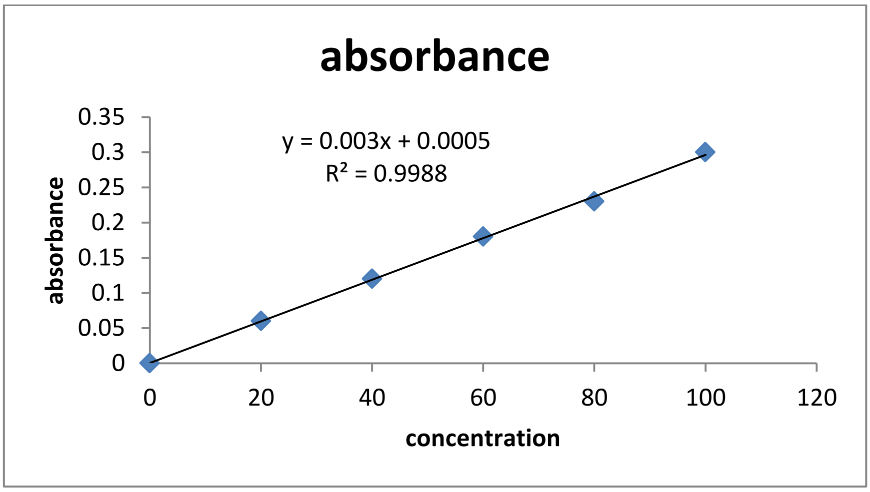

Figure3: Calibration curve for metal ion (Cu)

3.7. Characterization of Hydrogels(Chitosan Beads)

Chemical functional groups of chitosan were examined by FT-IR(Fourier transform infrared radiation) using KBr pellet method at room temperature. The spectra were find in the wave number range from 400 to 4000 cm-1 with a resolution of 4cm-1 by an infrared spectrometer. The morphological characteristics of the samples were studied by using SEM.

3.8. Adsorption Kinetics

The kinetic study of adsorption in wastewater plays an key role because it affords important look into the reaction and mechanism of the reaction. The kinetic model have been used to explain the mechanism of a solute sorption from aqueous solution onto an adsorbent

1. Pseudo First Order Kinetic Model
2. Pseudo Second Order Kinetic Model

3.8.1. Pseudo First Order Model

The Pseudo first order kinetic model has been widely used to predict the metal and dye adsorption kinetics. The metal and dye adsorption kinetics following the pseudo first order model is given by

$$\frac{dq}{dt} = k1(qe - qt) \qquad (3)$$

Where k1 is (min^{-1}) is the rate constant of the pseudo first order adsorption, qt (mg/g) the amount of adsorption at time t (min) and qe (mg/g) is the amount of adsorption at equilibrium. After definite integration by application of the conditions qt=0 at t=0 and qt=qt at t=t, equation (3) becomes

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$$\log(qe - qt) = \log qe - (\frac{k1}{2.303})t \quad (4)$$

By plotting log(qe-qt) vs. t, the adsorption rate can be calculated.

3.8.2. Pseudo Second Order Model

The adsorption kinetic data can be further analysed using Ho's pseudo second order kinetics (Mckay and Ho, 1999 b,c). This is represented by:

$$\frac{dq}{dt} = k_2(qe - qt)^2 \quad (5)$$

integration of equation 3 and application of the conditions q_(t=0 at t=0 and q_t=q_t at t=t) then the equation (5) becomes

$$\frac{t}{q_t} = \frac{1}{(k_2 {q_e}^2)} + \frac{t}{q_e} \quad (6)$$

where k_(2)(g/(mg min)) is the rate constant, k_2 and q_(e)can be obtained from the intercept and slope.

3.9. Adsorption Isotherm

Adsorption equilibrium is established when the amount of solute being adsorbed on to the adsorbent is equal to the amount being desorbed the equilibrium adsorption isotherms were depicted by plotting solid phase concentration of (qe) against liquid phase concentration of Ce of solute adsorption isotherm explains the interaction between the adsorbate and adsorbent and is critical for design of adsorption process. The Langmuir, Freundlich and Temkin isotherms are the most frequently used models to describe the experimental data of adsorption. In these present work these isotherms were applied to investigate the adsorption process of metal ions and dyes on chitosan at different conditions of process parameter.

3.9.1. Langmuir Isotherm Model

The Langmuir adsorption is the best model among the entire isotherm model and it is successfully applied in many adsorption processes. The Langmuir equation is given by

$$q_e = \frac{k_L q_m c_e}{1 + k_L c_e} \quad (7)$$

The linearization of it gives the following form

$$\frac{c_e}{q_e} = \frac{1}{q_m k_L} + \frac{c_e}{q_m} \quad (8)$$

Where c_e, equilibrium metal and dye concentration, q_m and k_L are the Langmuir constants related to maximum adsorption capacity (mg/g), and the relative energy of the adsorption (l/mg), respectively.

3.9.2. Freundlich Isotherm Model

The Freundlich isotherm model is one of the most widely used mathematical model which fit the experimental data over a wide range of concentration. These isotherm model are based on heterogeneous surface, distribution of active sites and their energies and enthalpy changes logarithmically. The Freundlich equation is given by (singh et al., 2011)

$$q_e = k_F c_e^{\frac{1}{n}} \quad (9)$$

the logarithmic form of equation is

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad (10)$$

where q_e is the amount of metal ion and dyes adsorbed after adsorption for specific amount of adsorbent (mg/g), C_e is the equilibrium concentration (mg/l), K_F and n are Freundlich equilibrium constants.

3.9.3. Temkin Isotherm model

Temkin isotherm contains a factor that clearly taking into the account of adsorbent-adsorbate interaction. The model assumes that heat of adsorption (function of temperature) of all molecules in the layer would decrease linearly rather than logarithmic with coverage on ignoring the extremely low and large value of concentration. Temkin isotherm is given by the following equation (Temkin and Pyzhev, 1940)

$$q_e = \frac{RT}{b} \ln(aC_e) \quad (11)$$

Linear form of this model is given by the following equation

$$q_e = a + b \ln C_e \quad (12)$$

where q_e is the amount of metal ion and dye adsorbed per specific amount of adsorbent (mg/g), C_e is the equilibrium concentration (mg/l), a is the equilibrium binding constant of (g^(-1)) and b is related to heat of adsorption(J/mol)which are Temkin constants.

4. RESULTS AND DISCUSSION

4.1. DYES

4.1.1. EFFECT OF PARAMETERS

4.1.1.1. EFFECT OF CONTACT TIME

From the figure 4 it can be seen that the %adsorption increases with increase in contact time for removal of dye till equilibrium is reached. The optimum contact time was found to be 180 minutes after this time the %adsorption remains constant. The amount of dye removed was found to be 85%.The dye removal efficiency of ECH cross linked beads showed higher adsorption capacities.

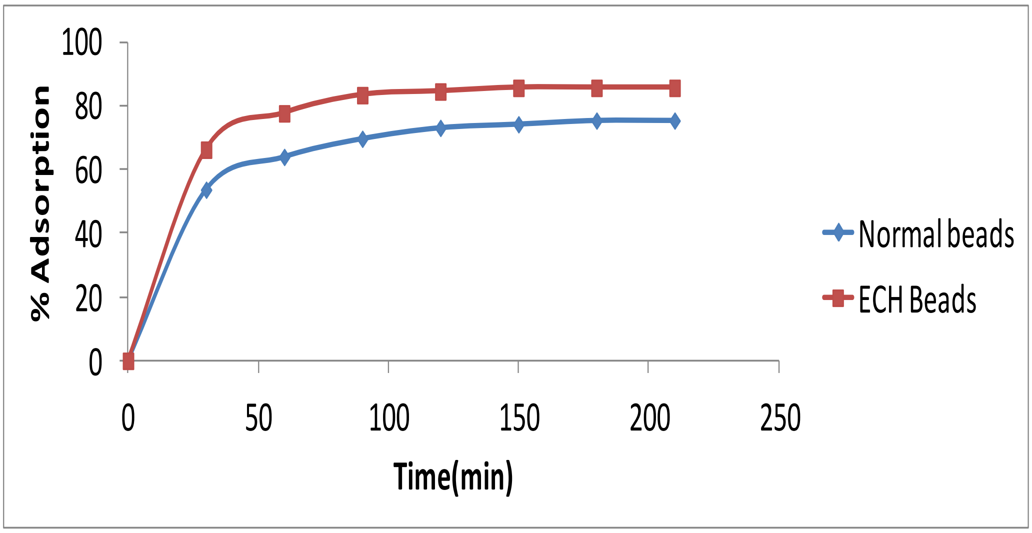

Figure 4: Effect of contact time on adsorption of dye

4.1.1.2. EFFECT OF PH

The pH of dye solution were varied from 2.5 to 6.5. The results indicate that dye removal is increased to maximum and then decreased with pH variation at room temperature. The dye adsorption was maximum at pH 4 and 5. Figure 5 shows the dye removal capacity of ECH cross linked beads, here non cross linked beads were not used because at lower pH the beads cannot withstand after certain time they dissolve and disappears in acidic medium.

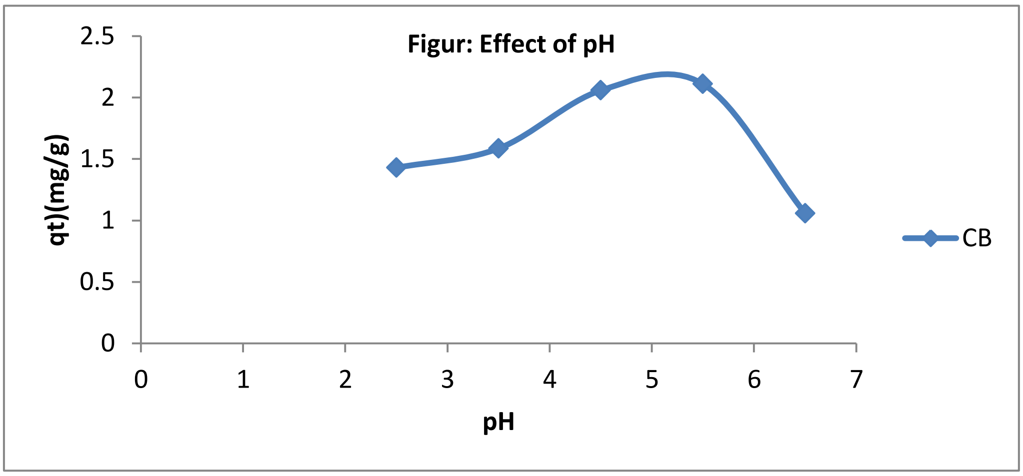

Figure 5:

Effect of pH on adsorption of dye

4.1.1.3. EFFECT OF INITIAL DYE CONCENTRATION

The dye solution of different concentrations of dye, that is 10,20,30,40 and 50 mg/litre were prepared using distilled water in laboratory and the extent of adsorption was observed. From the figure 6 and 7 it can be seen that the amount of dye removed increases with decrease in the concentration of dye. The amount of adsorbent used was

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kept constant that is 1g. At lower concentration of dye the adsorption was achieved almost complete. ECH cross linked beads shows a higher percent removal of dye as compared to normal beads.

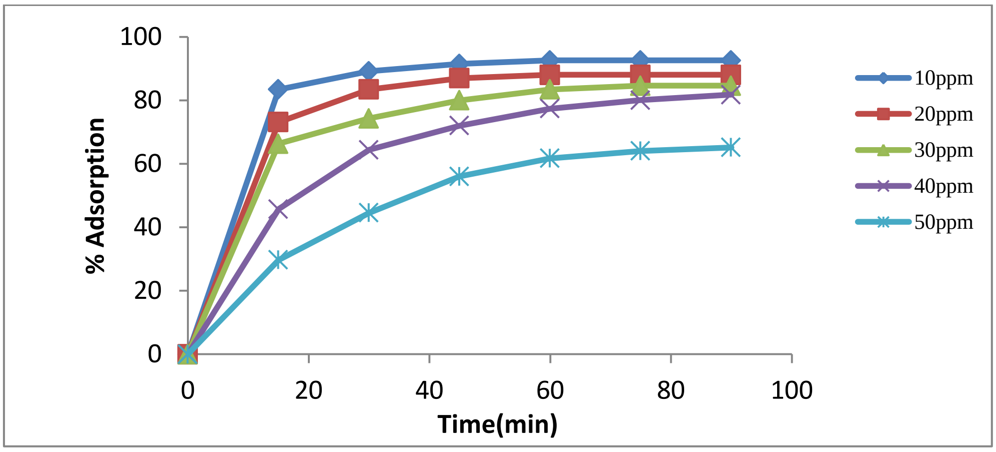

Figure 6: Effect of initial dye concentration on adsorption of dye onto ECH crosslinked chitosan beads

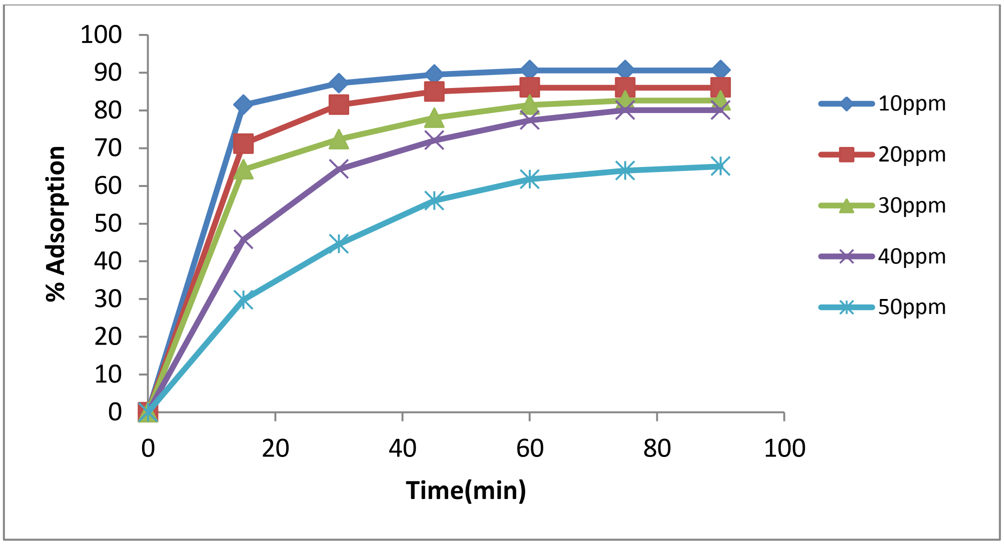

Figure 7: Effect of initial dye concentration on adsorption of dye onto normal chitosan beads

4.1.2. ADSORPTION KINETICS

The kinetics of adsorption was studied for a contact time ranging from 10-180 minutes. The experimental data was fitted to the pseudo first and second order kinetics model. The reported R^2 value indicates that the experimental results shows better fit to pseudo second order model. Hence, the dye adsorption on to the both normal and ECH cross liked beads seems to be more pseudo second order.

It is essential to know the adsorption isotherm so as to relate the effectiveness of different adsorbents under different operational conditions and also to design and optimize an adsorption system. In this project three isotherm models were used, Langmuir, Freundlich, Temkin isotherms using equations (8)(10) (12) respectively. The values of these models were calculated and tabulated in Table 2 given below. Langmuir, Freundlich and Temkin adsorption isotherms is presented in figure below, it shows that the experimental data fitted well to all the isotherm models. From the correlation coefficients, it was observed that Langmuir isotherm model well fits to the values when compared to others, which means that a monolayer adsorption of dye has occurred on hydrogels.

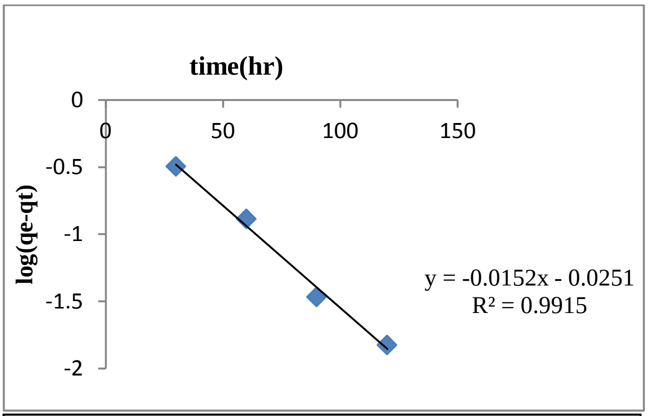

figure 8: ***Pseudo second order kinetics plot for dye adsorption without ECH***

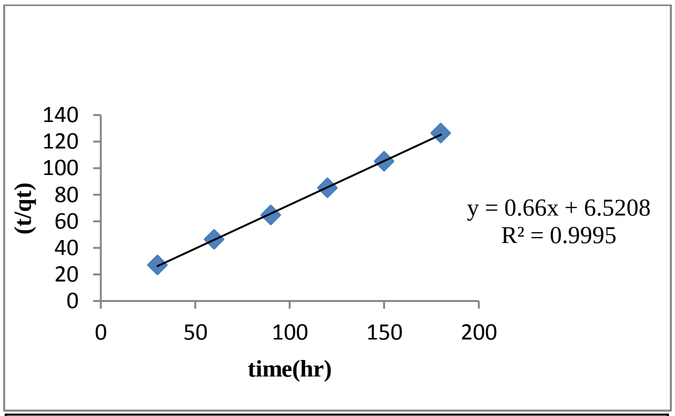

figure 9: ***Pseudo second order kinetics plot for dye adsorption with ECH***

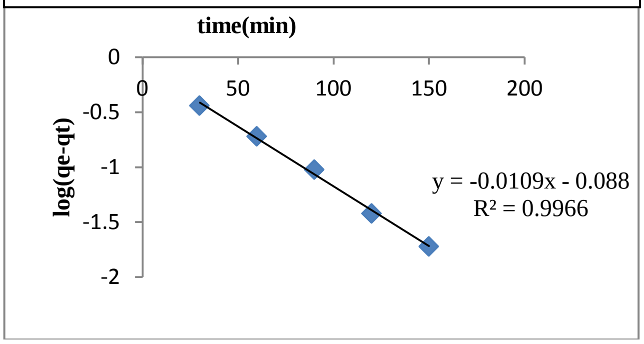

figure 10 :Pseudo first order kinetics plot for dye adsorption on normal beads

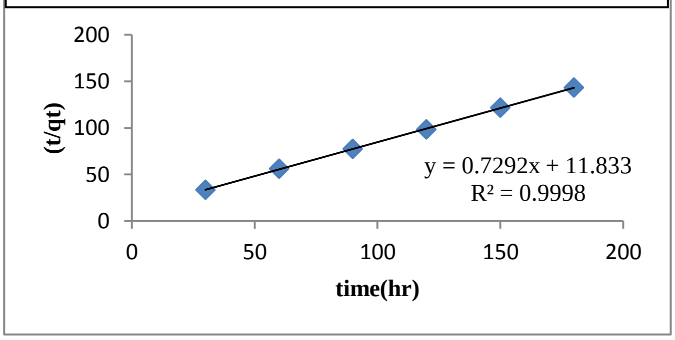

figure 11:Pseudo second order kinetics plot for dye adsorption on normal beads

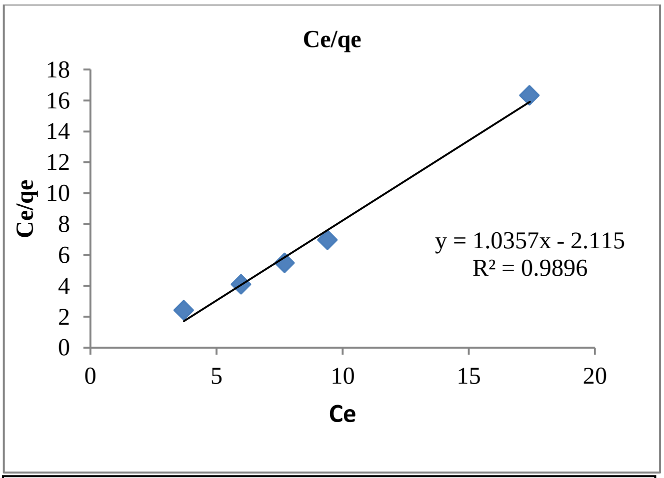

figure 12: ***Langmuir isotherm for chitosan beads***

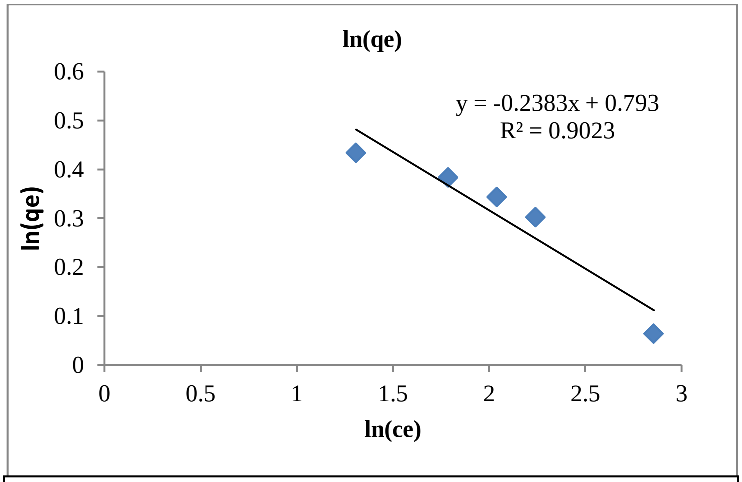

figure 13:Frendlich isotherm for chitosan beads

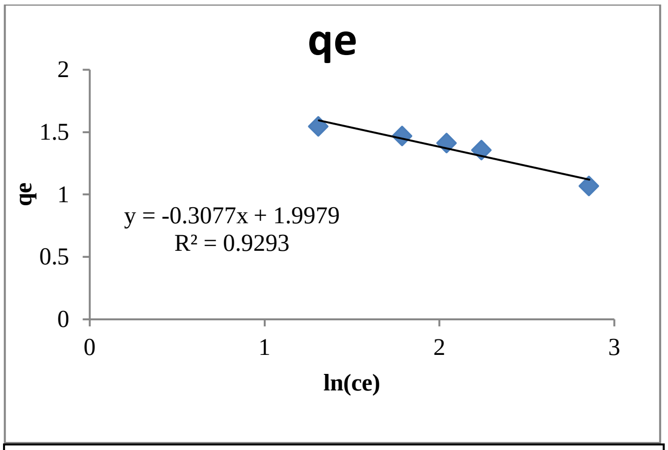

Figure 14: Temkin isotherm for chitosan beads

Table 2: Isotherm Constants for dye adsorption

ISOTHERMS	**VALUES**
Langmuir	
q_m(mg/g)	0.9655
K_L(L/mg)	0.489
R^2	0.9896
Freundlich	
K_F(mg/g)	2.21
N	4.196
R^2	0.9023
Temkins	
A	1.9979
B	0.3077
R^2	0.9293

4.1.4. COPPER OXIDE-CHITOSAN NANOCOMPOSITE HYDROGELS

4.1.4.1. Effect of initial concentration of dye

The extent of adsorption was observed with change in the initial concentration of dye. From the figure 15 it can be seen that the amount of dye removed increases with decrease in the concentration of dye. The initial concentration of dye was adjusted from 10 to 50 mg/L with the constant adsorbent dosage of 1g. At lower concentration of dye the adsorption efficiency was calculated to be 94.25%.

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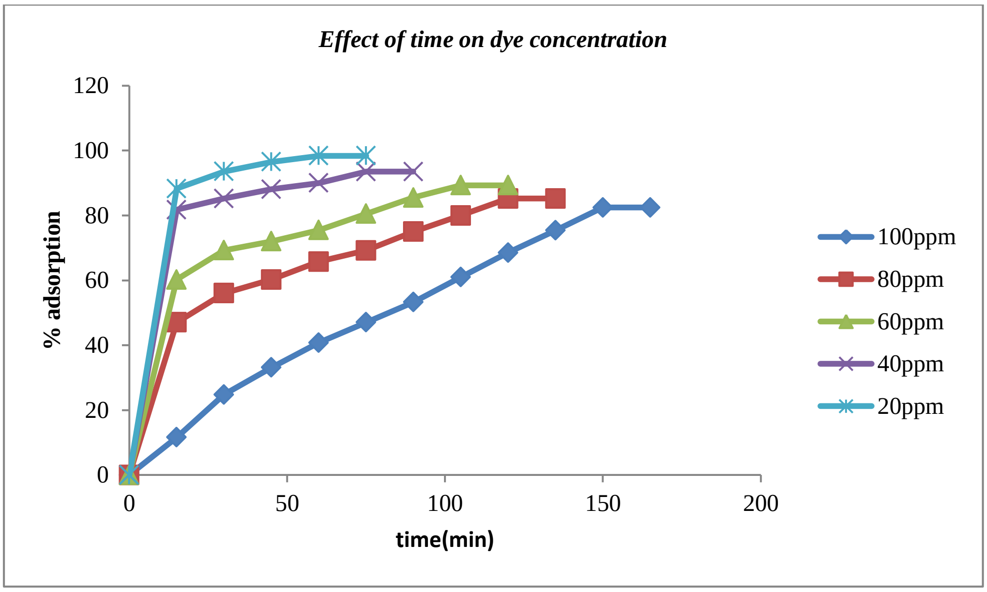

Figure15: Effect of initial dye concentration on adsorption of dye onto copper oxide chitosan nano composite beads

4.1.4.2. Effect adsorption dosage on adsorption

Adsorption efficiency of red dye adsorption was studied by varying the amount of adsorbents from 0.5-1.5 g keeping other parameters constant. The figure 16 shows that the removal efficiency of the copper improved on increasing the adsorbent dosage. This may occur due to the fact that the higher dosage of adsorbent in the solution provide the greater ability of exchangeable sites for the adsorption

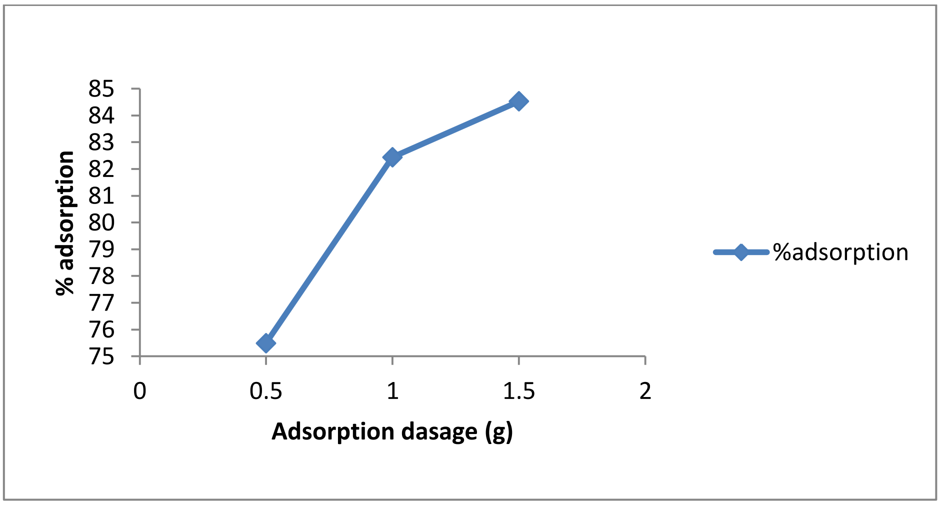

Figure16: Effect of adsorption dosage on adsorption of dye

Table 3: Comparison of the results of the hydrogels (chitosan beads) and nano particles incorporated hydrogels

HYDROGELS	Initial concentration of dye	% Adsorption values
Normal Beads	50 mg/L	75.46%
ECH cross linked Beads	50 mg/L	85.74%
Copper Oxide-chitosan nano composite	100mg/L	82.43%

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4.2. COPPER

4.2.1. EFFECT OF PARAMETERS

4.2.1.1. Effect of Time on adsorption of Copper Ions

From the figure 17: it can be seen that the %adsorption increases with increase in contact time for removal of Cu(II) till equilibrium is reached. The optimum contact time was found to be 8 hours after this time the %adsorption remains constant. The amount of dye removed was found to be 83.5.The dye removal efficiency of ECH cross linked beads showed higher adsorption capacities.

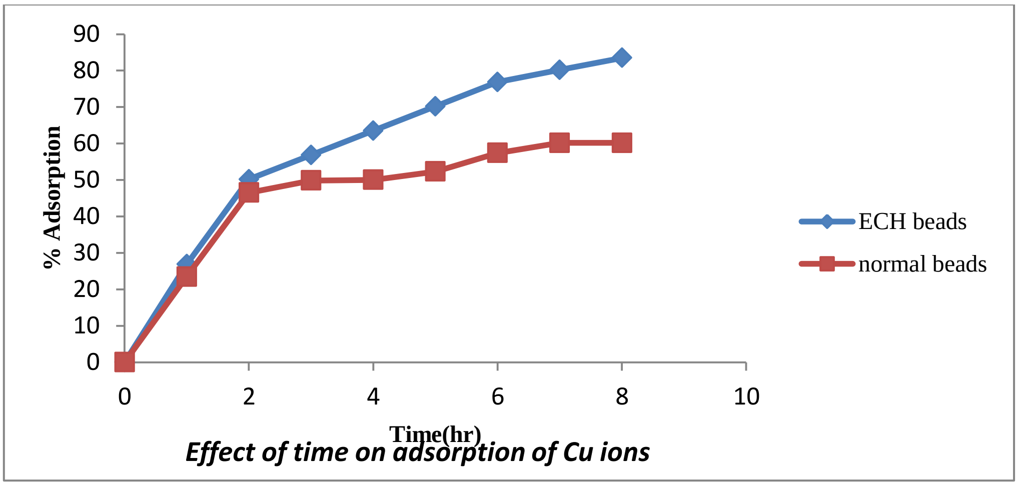

Figure 17: Effect of time on adsorption of copper ions

4.2.1.2. Effect of Adsorbent Dosage

Adsorption efficiency of Cu(II) adsorption was studied by varying the amount of adsorbents from 0.5-1.5 g keeping other parameters constant. The figure 18 shows that the removal efficiency of the copper improved on increasing the adsorbent dosage. This may occur due to the fact that the higher dosage of adsorbent in the solution provide the greater ability of exchangeable sites for the ions.

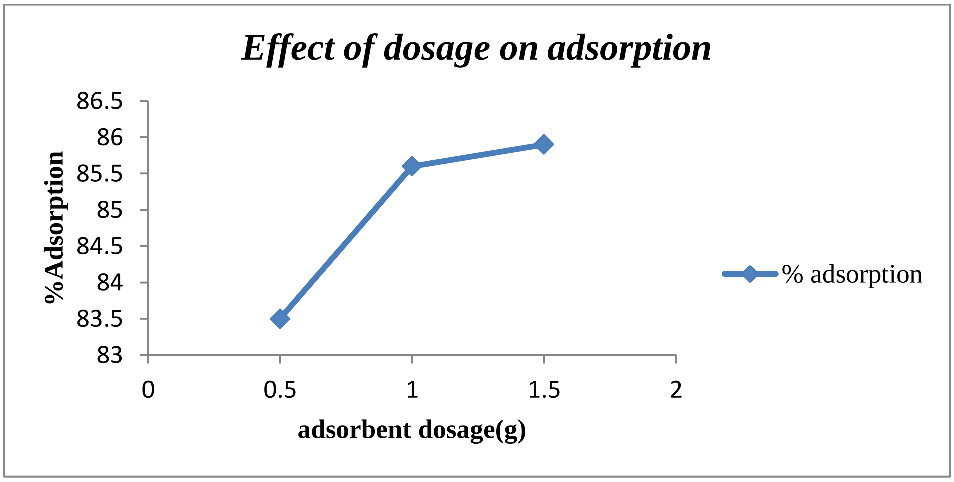

Figure 18: Effect of adsorbent dosage on adsorption of cu ions

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4.2.1.3. Effect of pH

The pH of dye solution were varied from 4 to 8. The results indicate that copper ion removal is increased to maximum and then decreased with pH variation at room temperature. The dye adsorption was maximum at pH 6. Figure 19 shows the copper ion removal capacity of ECH cross linked beads, here non cross linked beads were not used because at lower pH the beads cannot withstand after certain time they dissolve and disappears in acidic medium.

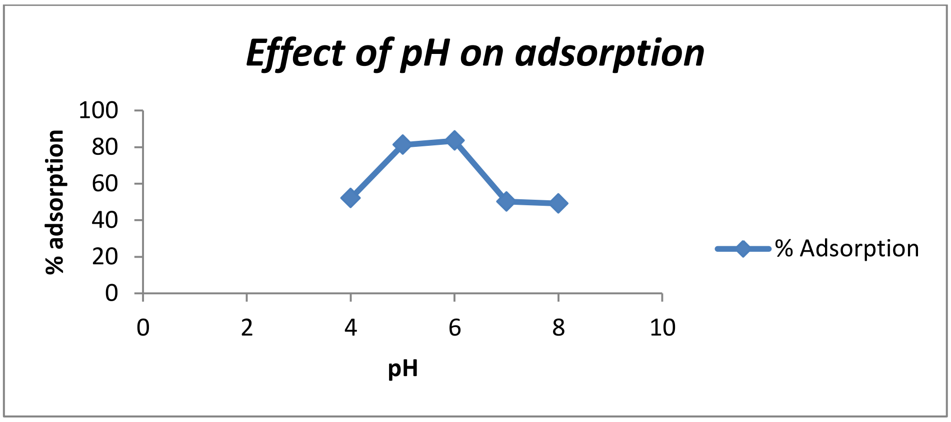

Figure 19: Effect of pH on adsorption of cu ions

4.2.1.4. Effect of initial metal ion concentration

The Cu(II) solution of different concentrations of dye, that is 20,40,60,80 and 100 mg/litre were prepared using distilled water in laboratory and the extent of adsorption was observed. From the figure 20 it can be seen that the amount of metal ions removed increases with decrease in the concentration of dye. The amount of adsorbent used was kept constant that is 1g. At lower concentration of dye the adsorption was achieved almost complete. ECH cross linked beads shows a higher percent removal of metal ions as compared to normal beads.

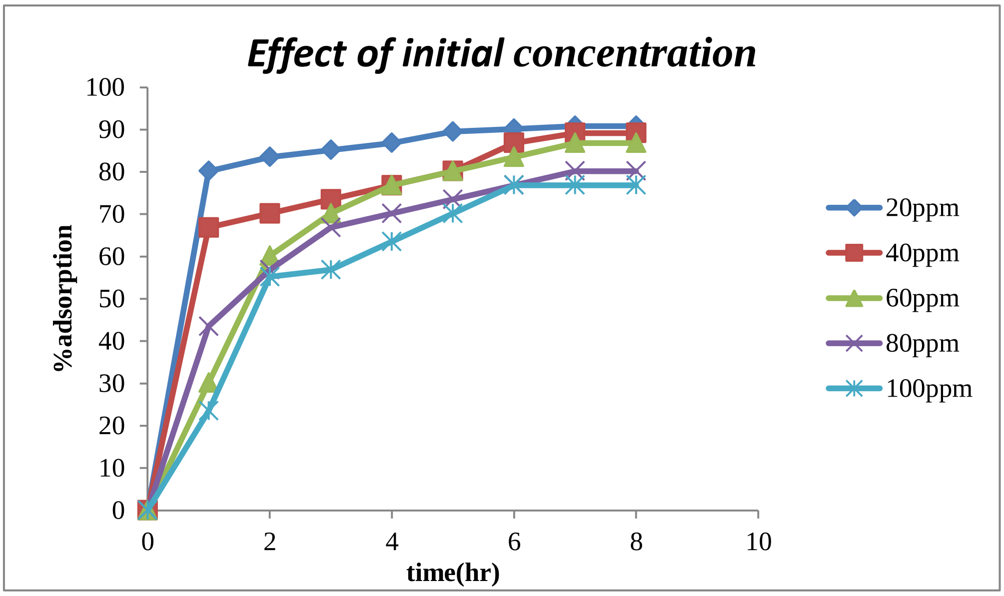

Figure 20: Effect of initial concentration of cu ions

Online ISSN: 2456-883X

4.2.3. ADSORPTION ISOTHERM

It is essential to know the adsorption isotherm so as to relate the effectiveness of different adsorbents under different operational conditions and also to design and optimize an adsorption system. In this project three isotherm models were used, Langmuir, Freundlich, Temkin isotherms using equations (8)(10) (12) respectively. The values of these models were calculated and tabulated in Table 4 given below. Langmuir, Freundlich and Temkin adsorption isotherms is presented in figure below, it shows that the experimental data fitted well to all the isotherm models. From the correlation coefficients, it was observed that Langmuir isotherm model well fits to the values when compared to others, which means that a monolayer adsorption of copper ions has occurred on hydrogels.

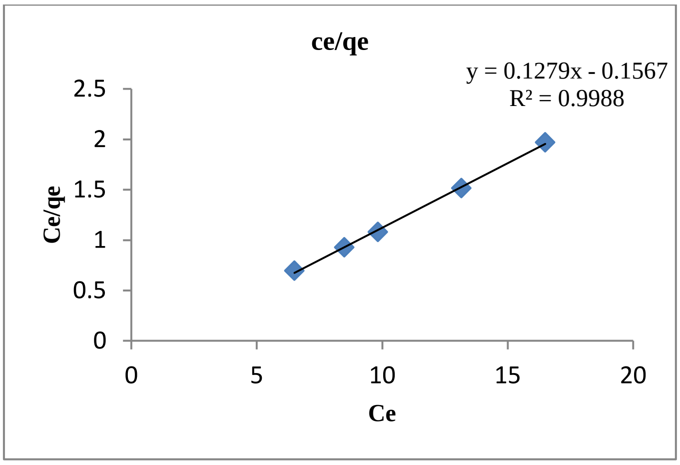

figure 21: Langmuir Adsorption isotherm for Cu adsorption

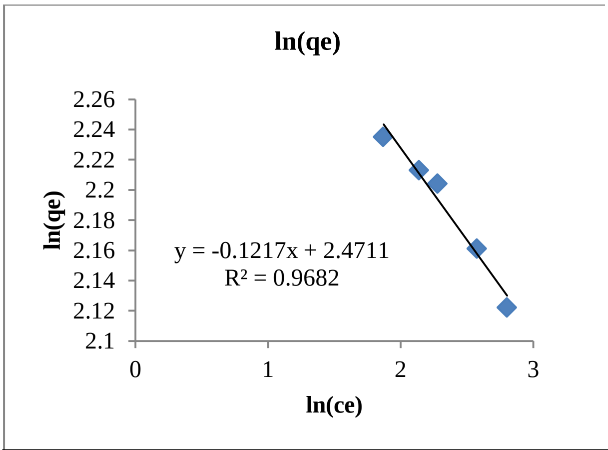

figure 22:Freundlich Adsorption isotherm for Cu Adsorption

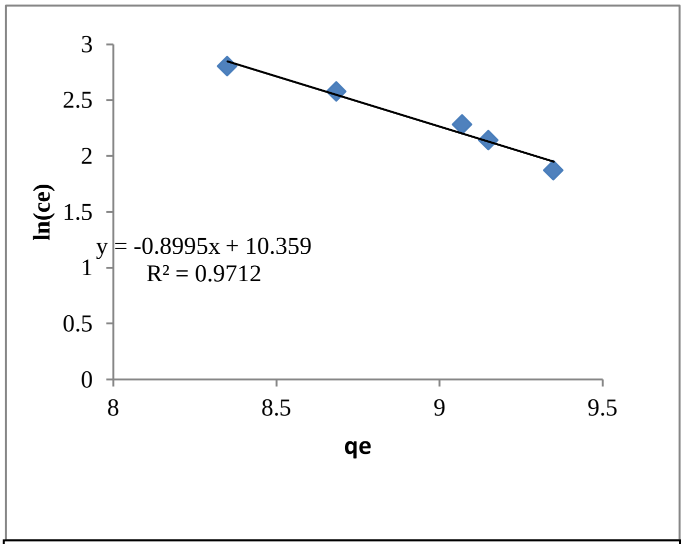

figure 23: Temkin adsorption isotherm for Cu adsorption

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Table 4:

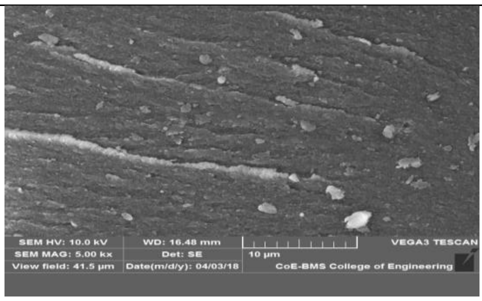
Isotherm Constant for Cu adsorption

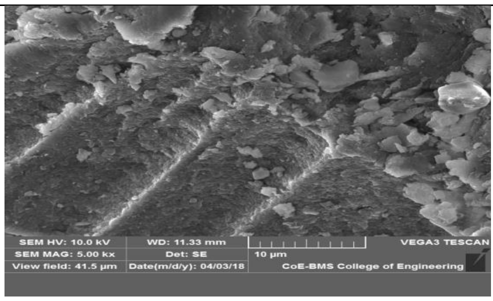
ISOTHERMS	VALUES
Langmuir	
q_m (mg/g)	7.818
K_L (L/mg)	0.816
R^2	0.9988
Freundlich	
K_F (mg/g)	1.13
N	8.217
R^2	0.9682
Temkin	
A	10.359
B	0.899
R^2	0.9712

5. CHARECTERIZATION OF SAMPLE

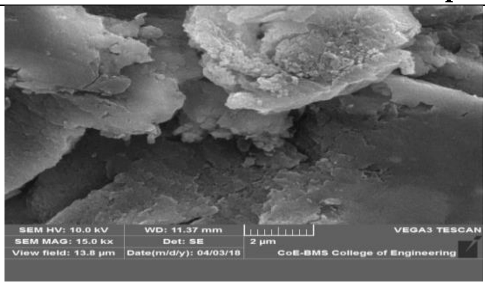
Surface morphology of synthesized hydrogels is determined by scanning electron microscope (SEM) images. SEM images for different hydrogels before and after adsorption of dyes are as shown below. ECH crosslinked beads before adsorption

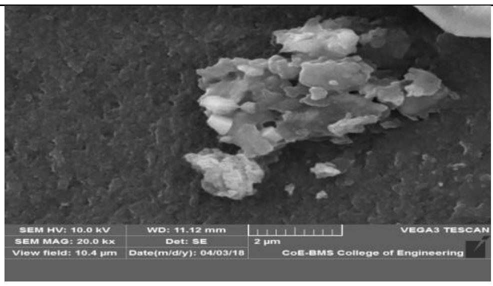
ECH crosslinked beads before adsorption





ECH cross linked beads after adsorption





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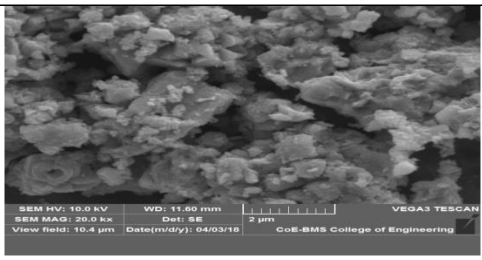
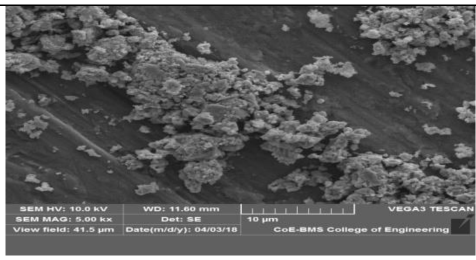
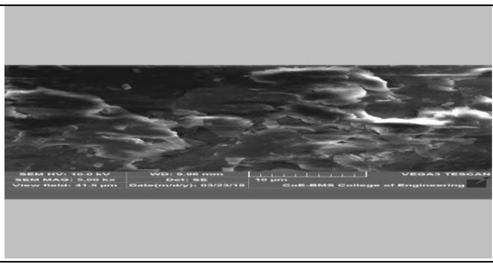
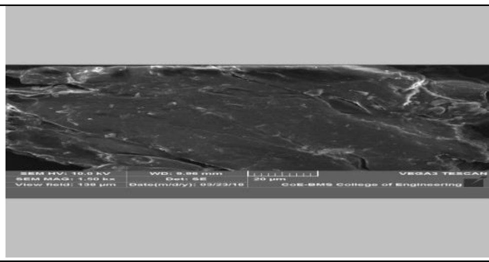
Normal beads After adsorption



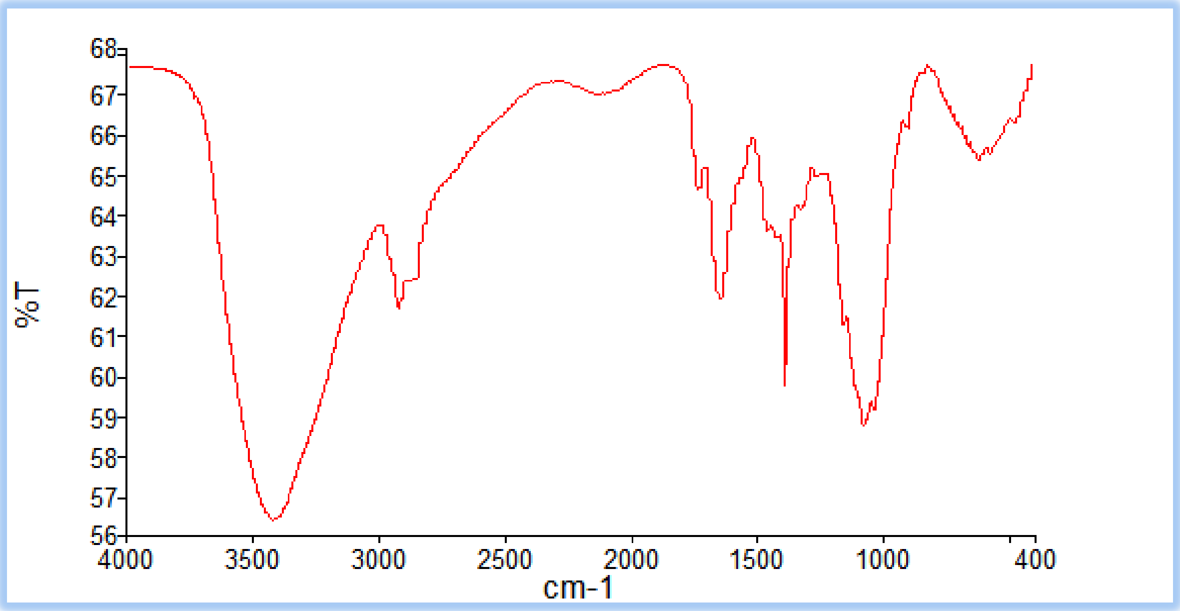


Normal beads before adsorption





The FT-IR graph of ECH crosslinked chitosan is presented below.



The specific adsorption band at 3435.63Cm-1 was attributed to the stretching vibration of O-H and N-H Bonds. The characteristic peak appeared at 1384 Cm-1 corresponding to the stretching of C-N of -NHCO, While the peaks at 1069.83Cm-1 and 2924.33cm-1 were belongs to C-OH bond and C-H of alkyl group respectively. The region of spectrum of 2200cm-1 is attributed to alkyl group (C≡C).

The presence of hydroxyl group, Carboxyl group and aromatic compounds is an evidence of the lignocellulosic structure of chitosan. Especially there was a new typical peak at 1647.54cm-1 confirming the formation of ECH crosslinking as a result of Schiff base reaction between -NH2 of Chitosan and -C=O of ECH.

6. CONCLUSION

Normal chitosan beads and ECH cross linked beads were successfully able to adsorb Congo red dye and heavy metal such as copper from the waste water. The removal of dye from waste water in the presence of Copper oxide was rapid at the during the initial stage followed by very slow adsorption rate. The efficiency of adsorption of Congo red dye was in the following order: Normal beads<ECH cross linked beads<CuO-chitosan beads. The optimum pH for the solution for dye and copper ions removal were found to be 5 and 6 respectively. The optimum time for the adsorption of dye and copper ions were found to be 180 min and 8 hours. Kinetic studies of adsorption revealed that the adsorption process followed a pseudo second order kinetic model for both dye and metal ions. The adsorption data were fitted to different isotherms model equation and the Langmuir model was found to be best model for both dye and metals.

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