

SORPTION OF ALIZARIN RED S DYE BY CHITOSAN IN MEMBRANE AND BULK FORM

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ABSTRACT

Chitin and chitison are naturally abundant and renewable polymers have excellent properties such as biodegradability, biocompatibility, and non-toxicity. Chitosan itself chelates metal ion especially those transition metal. It can be used for immobilization of enzymes. In the present work, chitosan is immobilized in Alizarin Red-S dye.

Methods: Take one gram of chitosan powder in conical flask. the homogenization of mixture in ultra Sonicator for 8- 10 hours. Keep the Petri plate along with solution in the oven for 24 hour at 50⁰C. Due to heating treatment in the oven the transparent film formed in the Petri-plate. After 24 hours the chitosan film was removed from the Petri plate. Wash with distilled water 2-3 times. **Result:** Immobilization of

alizarin red S dye in natural chitosan in bulk form and film form Alizarin Red S dyes shows absorption maxima at 530nm. This absorbance was measured using colorimeter and was used to study the immobilization of the dye in the film.. Immobilized chitosan film is used for immobilization of Fe (II) with Alizarin Red-S dye. To check the intake capacity of chitosan film UV-Spectrophotometer is used.

KEYWORDS: Chitin, chitison, Alizarin Red-S dye, UV-Spectrophotometer.

INTRODUCTION

Chitin is the second most ubiquitous natural polysaccharide after cellulose on earth and is composed of B (1-4) linked to acetoamino-2-deoxy-B-D-glucose (N- acetyl glucosamine). It is often considered as cellulose derivative, even though it does not occur in organism producing cellulose. It is structurally identical to cellulose but it has acetamide groups (-NHCOCH₃) at C-2 positions. Chitin is a white, inelastic, hard, nitrogenous polysaccharide

found in the exoskeleton as well as in the internal structure of in vertebrates. The waste of this natural polymer is major source of surface pollution in coastal area. The production of chitosan from crustacean shells obtained as a food industry waste is economical feasible, especially if it includes the recovery of carotenoids.

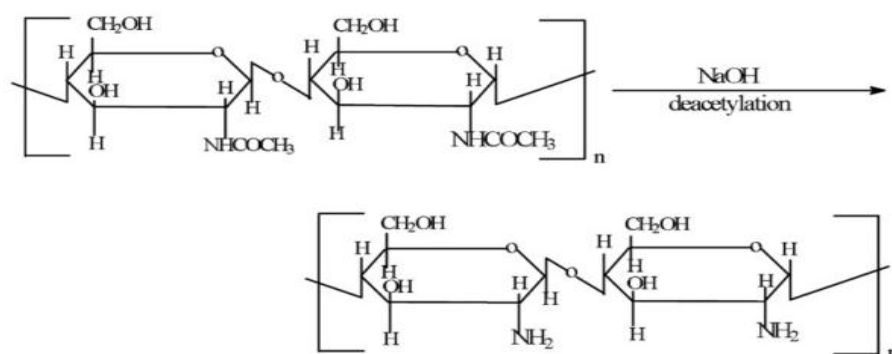


Fig. 1. Eactylation of Chitin to form Chitosan.

Derivatives of chitin and chitosan: Chitin and chitosan are naturally abundant and renewable polymers have excellent properties such as, biodegradability, biocompatibility, non toxicity, and adsorption. Chitosan is only soluble in aqueous solution of some acids and some selective N- alkyldination and N- acylation. Derivatives of chitosan may be classified into two categories and exposed amino function then reacts either with acyl chlorides or anhydrides to give the group (-NHCOR) or is modified by reductive amination to (-NHCH₂COOH) of greatest potential importance are derivatives both types formed by reaction with bi- or polyfunctional reagents, thus carrying sites for further chemical reaction.

Chitosan itself chelates metal ion specially those transition metal. And also find application as a matrix immobilization of enzymes. Reactions with pure chitin have been carried out mostly solid state owing to lack of solubility in ordinary solvents. A 50% deacetylated chitin has found to be soluble in water. This water soluble form of chitin is useful starting material for smooth modification through various reactions in solution phase.

METHOD OF PREPARATION

Preparation of solution of reagents

1. Alizarin Red S (ARS) (10^{-3} M)

0.0006 gm of Alizarin red S dye was weighed accurately and dissolved in distilled water. Transfer to a 100 ml volumetric flask and diluted upto the mark with distilled water. This solution was used as stock solution of a dye.

2. Sodium Hydroxide (0.01 N)

0.0389 gm of NaOH was weighed accurately and dissolved in distilled water. Transfer to a 100 ml volumetric flask and diluted upto the mark with distilled water.

3. Hydro chloric acid (0.01 N)

This solution was prepared by adding 0.36 ml of conc. HCl in distilled water. Transfer to 100 ml volumetric flask and diluted upto the mark with distilled water.

4. Ferrous Sulphate (1000 µg/ml)

0.496 gm of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was weighed accurately and dissolved in boiling distilled water. Transfer to 100 ml volumetric flask. This solution was used as stock solution of a dye. From this solution $100\mu\text{g} \cdot \text{ml}^{-1}$ was prepared by dilution with distilled.

Preparation of natural chitosan films

- 1 gm of chitosan powder was dissolved in 1% acetic acid solution.
- Then the solution was transferred to 100 ml volumetric flask and diluted up to the mark, with distilled water.

Following flow sheet diagram shows a preparation of chitosan film

- Take one gram of chitosan powder in conical flask and dissolved in 1% acetic acid
- Ultrasonicate for the dissolution and the homogenization of mixture in ultra Sonicator for 8- 10 hours.
- Pour the solution in the glass Petri-plate.
- Keep the Petri plate along with solution in the oven for 24 hour at 50°C
- Due to heating treatment in the oven the transparent film formed in the Petri-plate.
- After 24 hours the chitosan film was removed from the Petri plate. Wash with distilled water 2-3 times

Immobilization of alizarin red S dye in natural chitosan in bulk form and film form

Natural chitosan films were cut into 1 by 2 cm pieces and equilibrated with alizarin red S dye of various concentration. The films after immobilization of dye were taken out washed with water and stored for further used. Same treatment was given in the case of chitosan in bulk form. Various concentrations required for immobilization of ARS like concentration of dye, pH of dye solution, time required for complete immobilization were studied.

Variation of concentration of dye

In this study, 1 by 2 cm pieces of natural chitosan film were immersed into ARS solution containing 0.5 to 8 mg. The absorbance of dye solution was recorded on colorimeter, before immersing the films. The films were kept in the dye solution for fixed interval of time. The absorbance of the residual solution was recorded at regular interval of time. The change in absorbance of the dye before equilibration with film and after immobilization in the film (residual solution) was plotted as a function of amount of dye taken.

All absorbance measurement was done at 530 nm. Same experiment was carried out for the chitosan in bulk form.

Variation of time of immobilization of dye: In this study 1 by 2 cm piece of film was equilibrated with 10ml of 10^{-3} M of dye and the absorbance of residual solution was measured at different interval of time ranging from 5 minute to 8 days. This experiment was continued till constant values were obtained for residual solution. A plot of absorbance of residual solution as a function of time of equilibration was plotted.

Same experiment was carried out for the bulk form.

Variation of pH of aqueous solution using alizarin red S dye: The pH of alizarin red S dye was varied in the range of pH-2 to pH-12 and the absorption spectra for each solution was recorded. The pH adjustment was done using 0.01 N NaOH and 0.01 N HCL.

Determination of iron (II) in an aqueous solution using alizarin red S dye

Following procedure was used for determination of iron (II) in aqueous solution using alizarin red S dye. In the study iron (II) solution was taken in a range of 0.5-5 μ g/ml in 100 ml test tubes 2.5 ml 10^{-3} M. The alizarin red S was added in iron (II) solution. Final volume of solution was made up to 10 ml using distilled water. The absorbance of solutions was recorded on a colorimeter at wavelength 530nm.

Uptake of Iron (II) in alizarin red S immobilization alizarin chitosan film

A series of concentration of iron (II) in the range 0.5-5 μ g/ml was taken. A 1 by 2 cm piece of ARS immobilized film was immersed in each of iron concentration. After 20 minutes of reaction between iron (II) and ARS in the film, the film was removed and iron (II) in the residual solution was measured. A calibration curve of absorption value of Fe-ARS complex in residual solution VS amount of Fe (II) in equilibrating solution was plotted.

RESULTS AND FUTURE SCOPE

Immobilization of alizarin red S dye in natural chitosan in bulk form and film form Alizarin Red S dyes shows absorption maxima at 530nm. This absorbance was measured using colorimeter and was used to study the immobilization of the dye in the film. The dye on immobilization in the film makes the film turn to red color. The dye remains stable for a long period of time.

Following figure shows a photograph of ARS immobilized film.



Fig. 2. Photograph of ARS immobilized film.

Variation of concentration of dye

The change in absorbance of the before equilibration with film and after immobilization in the film was plotted as a function of amount of dye taken. From the graph it can be observed that the difference in absorbance value at 530nm increases linearly with increase in weight of alizarin from 0.2-1 mg and then remains constant till 5 mg. After 5mg it shows an increase. Thus it can be concluded that 0.5 gm of chitosan in bulk form can take about 5 mg ARS dye.

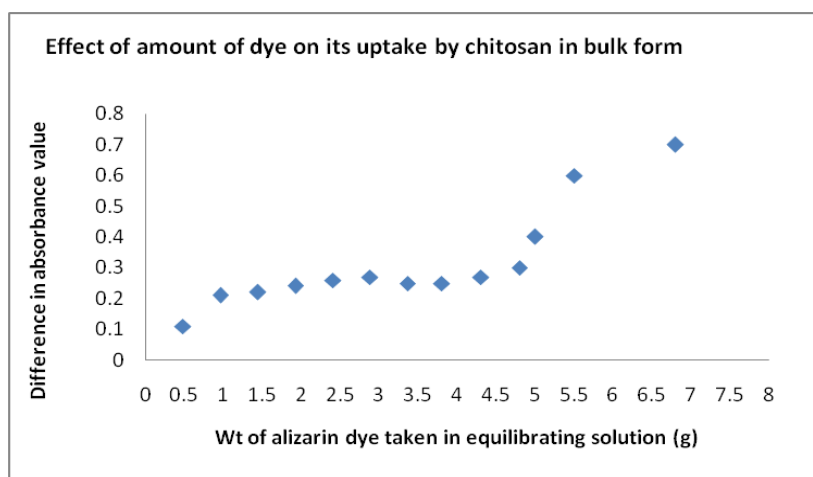
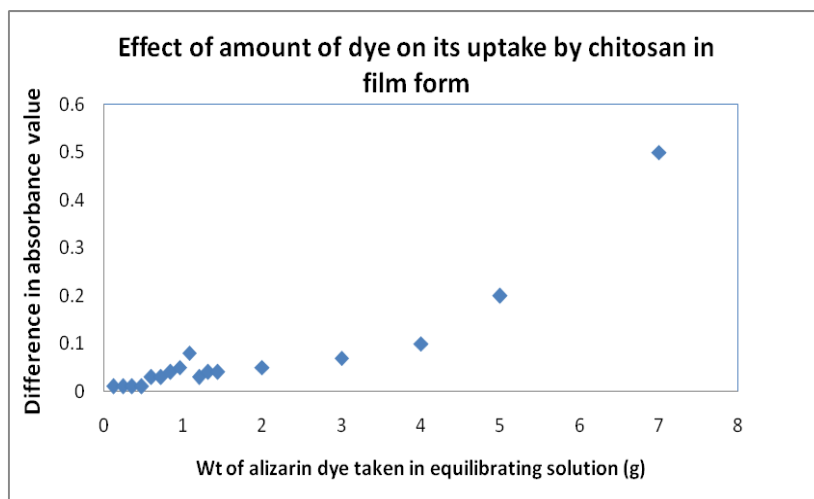
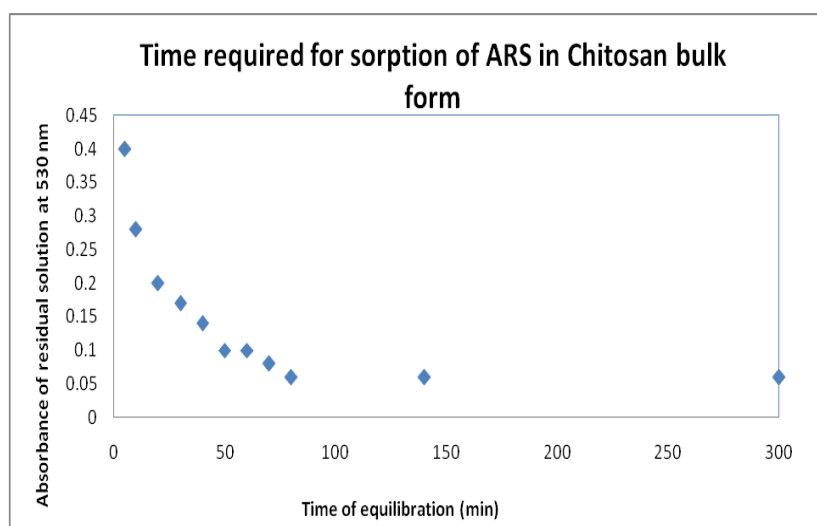


Fig. 3.

**Fig. 4.**

Variation of time of immobilization of dye

Figure 4 shows the variation of time of equilibration of film or powder with alizarin Red S dye solution. The time of equilibration is plotted amount VS absorbance of residual solution after removal of film or powder from the solution. It can be observed from the figure that the absorbance of residual solution decreases with increase in equilibration time and remains constant after 90 minutes. It can be concluded that the time required for complete immobilization is about 90 minutes. It was also observed that the films remain stable till 8 days. Same results were obtained for powder.

**Fig. 5.**

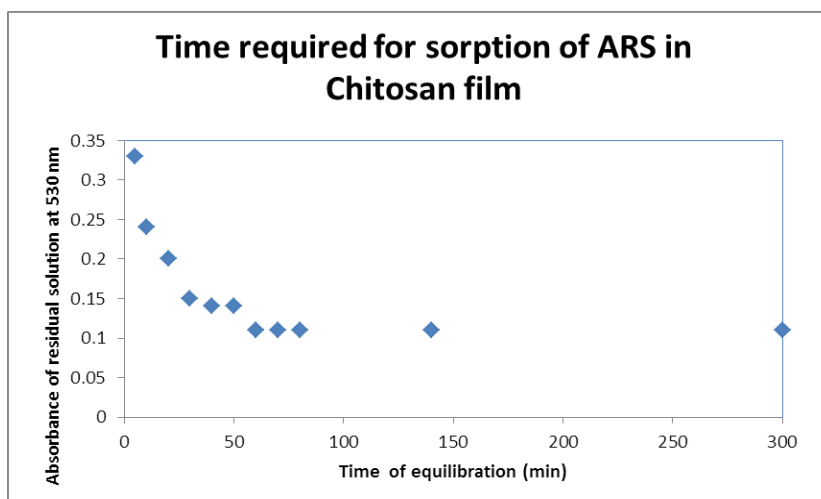


Fig. 6.

Variation of pH of aqueous solution of alizarin red S dye

Aqueous solution of alizarin red S dye shows different absorption maxima at different pH values. Following figure shows the spectra of alizarin red S solution at different pH values. It can be seen that the absorption maxima at different pH values are different for different pH values.

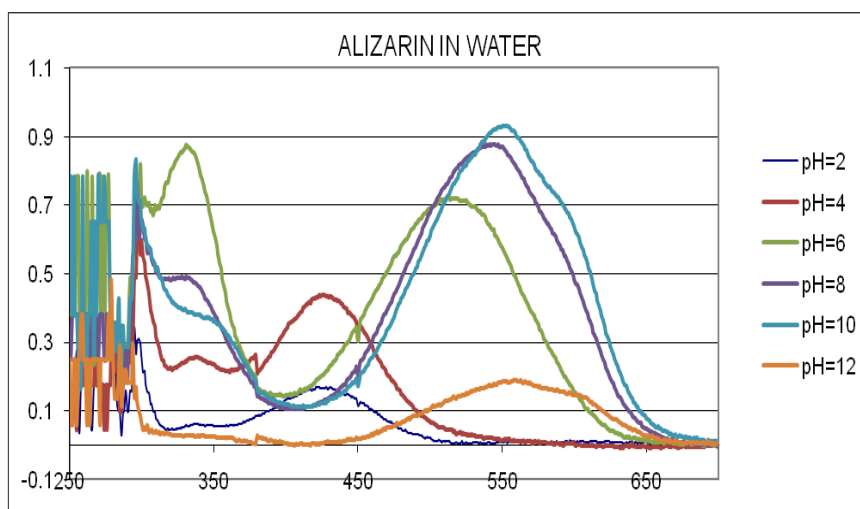


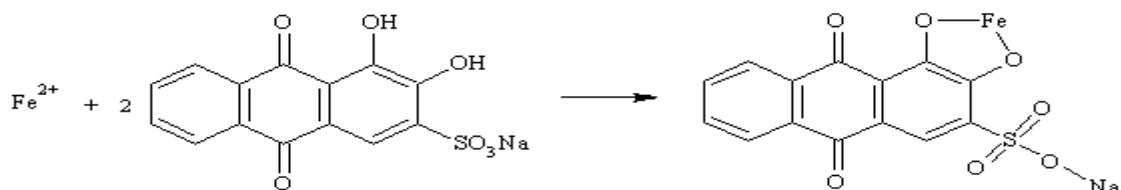
Fig. 7.

Determination of iron (II) in an aqueous solution using alizarin red S dye

Iron (II) and alizarin red s dye in neutral aqueous solution form a brown colored complex which shows absorption maxima at 560.6 nm.

Alizarin shows different absorption maxima at different pH values. Various metal ions can form different complexes with alizarin at different pH values

Following is a reaction of alizarin red S is with iron (II)



Linear calibration curve was obtained in the concentration range (0.5-5) $\mu\text{g/ml}$.



Fig. 8. Photograph of ARS and Fe immobilized film.

Use of alizarin red S immobilized chitosan films for uptake of iron (II) in an aqueous solution: Following figure shows absorbance value of Fe-ARS complex in residual solution VS amount of Fe (II) in equilibrating solution (μg). It is found that absorbance of resulting solution when treated with iron (II) varies linearly with the amount of iron taken in equilibrating solution. Thus this alizarin red s immobilized chitosan films can be used for uptake of Fe (II) from aqueous solution.

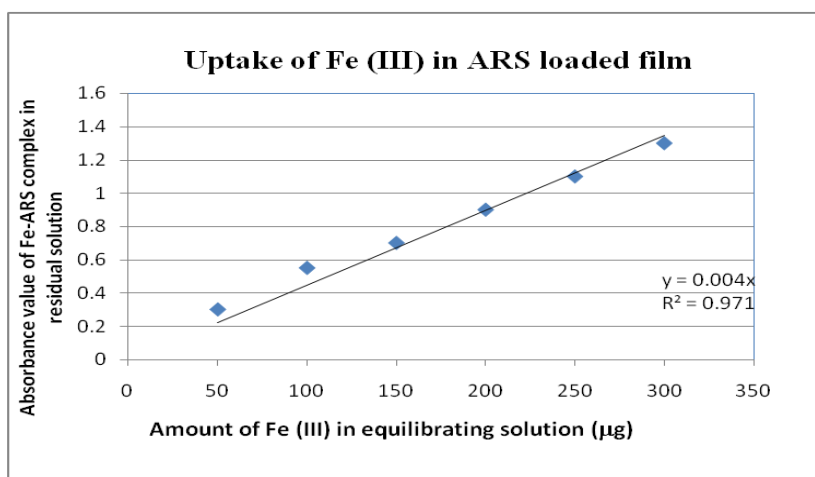


Fig. 9.

Alizarin red S dye can be immobilized in chitosan in both film and powder form. The dye remains stable in the film and in the powder for a long time.

Following photograph shows stability of alizarin dye in film and in powder form.



Fig. 10. Stability of alizarin dye in film and in powder form.

CONCLUSIONS

Following important conclusion can be drawn in the present work.

1. Alizarin red S dye can be immobilized in chitosan in both film and powder form. The dye remains stable in the film and in the powder for a long time.
2. The uptake capacity of film is found to be more than bulk form.
3. The ARS dye immobilized chitosan films can be efficiently used for the removal of various metals ions like Cr, Cd, Cu, Pb, Fe, Zn etc. In the present work ARS immobilized chitosan film have been used for uptake of Fe (II) from aqueous solution.

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