

## MAGNETIC CHITOSAN MICROSPHERES PREPARATION FROM BLACK SEA CRABS AND THEIR USE AS A NATURAL BIOPOLYMER ADSORBENT FOR COLOR WASTE WATER TREATMENT

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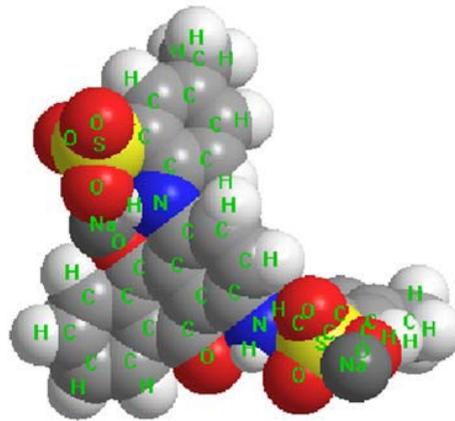
### ABSTRACT

A method of preparation of magnetic chitosan microspheres (MCM) has been investigated. In addition, its applications in the wastewater treatment, based on different kinds of wastewater, have been researched, and their mechanisms have been discussed. The preparation of MCM was precipitation method developed based on the special solubility characteristics of chitosan: dissolved in acidic aqueous media but precipitated in alkali one. In a definite condition, regular microspheres would be formed by adding chitosan solution dropwise to alkali aqueous solution. The magnetic chitosan microspheres obtained are investigated for color waste water from paper and textiles industries. Their magnetic properties allow a good separation after the waste water purification processes. The results obtained show an effective use in waste treatment field.

*Key words: chitosan microgranule, FTIR spectroscopy, water purification*

### INTRODUCTION

Dyes are widely used in various industries such as dyestuffs, textiles, leather, papers, plastics, and the like. Unfortunately, dyes that remain in waste effluents undergo chemical changes, consume dissolved oxygen, and destroy aquatic creatures. Moreover, these dyes may cause suspected carcinogenic and genotoxic effects. However, due to the large degree of aromatic rings present in the dye molecules, the treatment of wastewaters via a biological process is difficult and ineffective, resulting in their being discharged into the environment [2]. In this light, a wide range of conventional treatment processes including coagulation, precipitation, membrane filtration, oxidation, adsorption, and photodegradation have been utilized for removing dyes from wastewater [2,3,8,9]. Among all wastewater treatments, the adsorption process has been recognized to be an effective and economical procedure for the removal of dyes from industrial effluents. A large variety of adsorbent materials have been tested to remove dyes including activated carbon, which is one of the most widely used adsorbents because of its excellent adsorption capacity for organic pollutants. Because it is very expensive, low-cost biosorbent materials with high adsorption capacities have gained increasing attention in reducing the adsorbent dose and minimizing the disposal problem. In connection with this, special attention has been given to polysaccharides such as chitosan, which is a natural aminopolymer. Specifically, chitosan is a linear polycationic polymer containing 2-acetoamido-2-deoxy- $\beta$ -D-glucopyranose and 2-amino-2-deoxy- $\beta$ -D-glucopyranose residues. It has served as one of the most popular adsorbents for the removal of dyes from an aqueous solution and has been widely used in waste treatment applications [1,4–7,10]. Although the crosslinking method may reduce the adsorption capacity of chitosan to remove dyes, it can enhance its resistance of chitosan against acids and chemicals. This may be attributed to the extent of crosslinking and the decreased amount of the amino group, which is expected to play a great part in the adsorption process. In the present study, the crosslinked chitosan microparticles were prepared from based on the formation of microparticles with  $\text{Fe}_3\text{O}_4$ . The crosslinked chitosan microparticles were then characterized using FTIR, they were used for adsorption of dyes, namely Acid Green 25 and Acid Green 27 in an aqueous solution (Fig. 1). This information would be useful for further applications in the treatment of waste effluents from the dye industry.



Acid Green 25

Fig. 1. Molecular structures of Acid Green 25.

### MATERIALS AND METHODS

2 g chitosan were dissolved in 100 mL 2% (v/v) of acetic acid solution after which the mixture was stirred for 1h at room temperature. Then 0.4 g maghemite ( $\text{Fe}_2\text{O}_3$ ) nanoparticles was added under stirring for 1 h. Subsequently, 2 mL 25% (v/v) glutaraldehyde as crosslinking agent was added dropwise. The emulsion was kept in a water bath at 40 °C for 1 h. 1 mol L<sup>-1</sup> NaOH was used to adjust pH to 9–10. Finally, the product was washed with N, N-dimethylformamide, ethanol and twice-distilled water for 3–4 times, respectively, and dried under atmospheric condition.



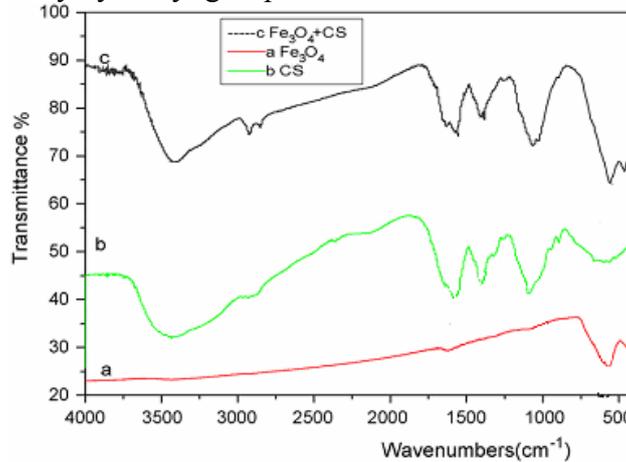
**Scheme 1.** The formation process of magnetic  $\text{Fe}_3\text{O}_4$ -chitosan nanoparticles.

To realize the binding mechanism, FTIR spectra of the naked  $\text{Fe}_3\text{O}_4$  (a), CS (b) and  $\text{Fe}_3\text{O}_4$ -chitosan nanoparticles (c) were examined as shown in Fig. 2. The peak around  $3440\text{ cm}^{-1}$  observed in curve b and c relates to the  $-\text{OH}$  group. For the naked  $\text{Fe}_3\text{O}_4$  (Fig. 2a), the peak at  $570\text{ cm}^{-1}$  relates to  $\text{Fe}-\text{O}$  group. For the IR spectrum of CS (Fig. 2b), the characteristic absorption bands appeared at  $1590\text{ cm}^{-1}$  which can be assigned to  $\text{N}-\text{H}$  bending vibration, peaks  $1400\text{ cm}^{-1}$  appeared to  $-\text{C}-\text{O}$  stretching of primary alcoholic group in chitosan. In the spectrum of  $\text{Fe}_3\text{O}_4$ -chitosan nanoparticles (Fig. 2(c)), compared with the spectrum of CS, the  $1590\text{ cm}^{-1}$  peak of  $\text{N}-\text{H}$  bending vibration shifted to  $1560\text{ cm}^{-1}$ , and a new sharp peak  $1630\text{ cm}^{-1}$  appeared, it indicated that chitosan react with glutaraldehyde to form *Schiff* base, and a new sharp peak  $560\text{ cm}^{-1}$  relates to  $\text{Fe}-\text{O}$  group appeared. The results indicated that CS was coated to the magnetic  $\text{Fe}_3\text{O}_4$  nanoparticles successfully.

#### *Effects of pH*

The effect of different pH on Acid Green 25 uptakes for three different pH values (6, 8 and 10) is shown in Fig. 3. The glucopyranose unit chitosan contains one amine group, one primary

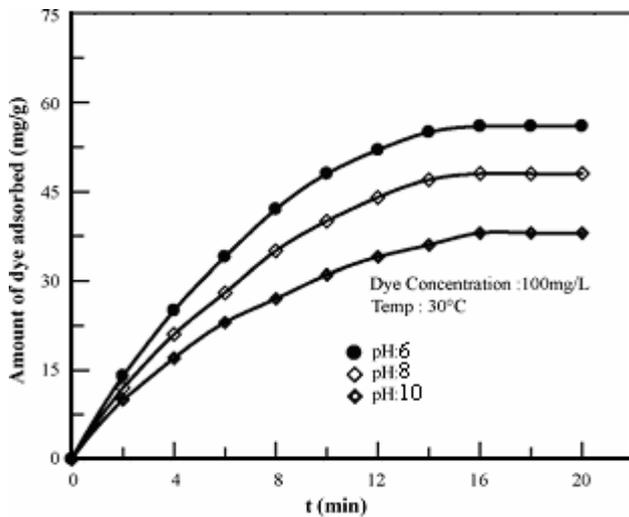
hydroxyl group (CH<sub>2</sub>OH) and two secondary hydroxyl group (OH), the dye tend to react preferentially with the primary hydroxyl group.



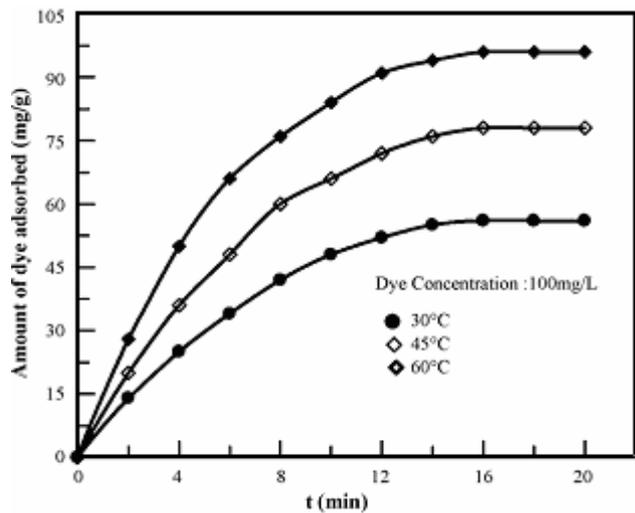
**Fig. 2.** FTIR spectra of the naked Fe<sub>3</sub>O<sub>4</sub> (a), CS (b) and Fe<sub>3</sub>O<sub>4</sub>-chitosan nanoparticles (c).  
*FTIR spectra analysis*

*Effects of pH*

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**Fig. 3.** Effect of specific dye uptake for different pH with time.

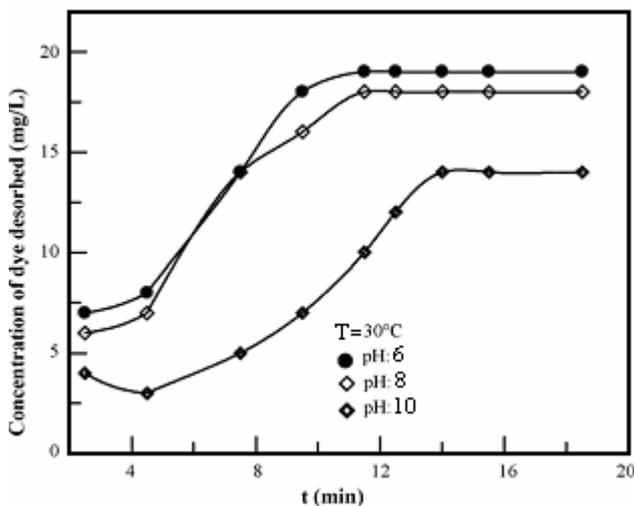


**Fig. 4.** Effect of specific dye uptake for different temperatures with time.

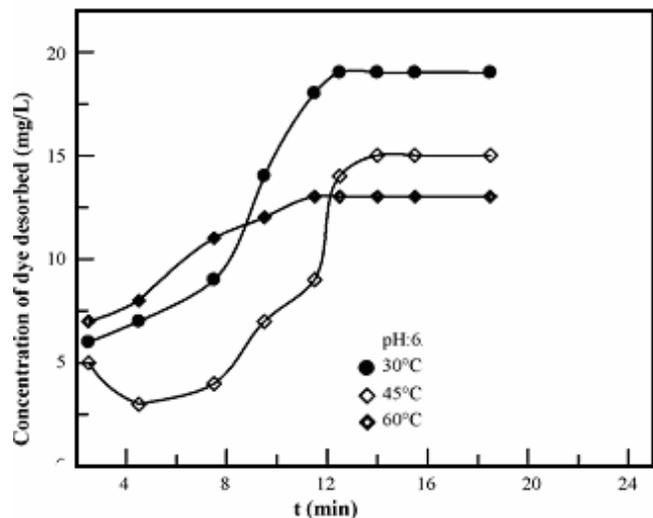
However, chemical reactions between the amine groups of chitosan and dye seen highly improbable. The maximum values for the adsorption capacity ratio between acidic and alkaline conditions reach 5–6.7 for Acid Green 25 on chitosan. At lower pH more protons will be available to protonate amine groups of chitosan molecules to form groups NH<sub>3</sub><sup>+</sup>, thereby increasing electrostatic attractions between negatively charged dye anions and positively charged adsorption sites, and causing an increase in dye adsorption. It can be seen that the pH of aqueous solution plays an important role in the adsorption Acid Green 25 onto chitosan.

*Effects of temperature*

Temperature is an important parameter for the adsorption process. A plot of the Acid Green 25 uptake as a function of temperature (30, 45 and 60 °C) is shown in Fig. 4. The results reveal that the dye uptake increased with increasing temperature at 30 °C 60.0 mg/g; 45 °C 80.0 mg/g and 60 °C 95.0 mg/g). The adsorption of dye at higher temperatures was found to be greater than that at a lower temperature. The curves indicate the strong tendency for the process for monolayer formation process to occur. The increase in temperature would increase the mobility of the large dye ions as well as produce a swelling effect with in the internal structure of the chitosan, thus enabling the large dye molecules to penetrate further. Therefore, the adsorption capacity should largely depend on the chemical interaction between the functional groups on the adsorbent surface and the adsorbate, and should increase as the temperature rises. This can be explained by an increase in the diffusion rate of the adsorbate into the pores. At higher temperatures the adsorbent might contribute to the adsorption of Acid Green 25, as diffusion is an endothermic process.



**Fig. 5.** Effect of pH on dye desorption.



**Fig. 6.** Effect of temperatures on dye desorption.

*Desorption and regeneration studies*

After confirming the fact that, chitosan is capable of adsorbing the dye onto its surface, it becomes necessary and imperative to know the nature, or the process, by which the dye remains adhered to the surface of the material. The nature of the adherence of the dye onto the surface of the material was purely chemical, involving chemical binding of the substances. The nature of bonding can be elicited by subjecting the adhered material to desorption and regeneration processes. In the present investigation, experiments were conducted to ascertain the nature of the binding of dye on to the material surface. The desorption of dye at different pH (6, 8, 10) and temperature (30, 45, 60 °C) values is shown in Figs. 5 and 6. The desorbed dye was found to be negligible; one may conclude that the binding of the dye onto the material under study may be purely chemical in nature. Chitosan is a naturally occurring material a chelating polymer. The presence of hydroxyl and amino groups in this polymer make it a potential adsorbent for textile dye effluents. It seems likely that adsorption mechanism may be as follows: first Acid Green 25 is dissolved in an aqueous solution after which the sulphonate groups of Acid Green 25 ( $R-SO_3Na$ ) become dissociated and converted to anionic dye ions.

## CONCLUSIONS

Magnetic Fe<sub>3</sub>O<sub>4</sub>-chitosan nanoparticles were fabricated by the covalent binding of CS on the Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The adsorption of dye from an aqueous solution using chitosan has been investigated, under different reaction conditions. Dye sorption at the external surface of the polymer represents a significant part of the sorption process. However, the decrease in sorption capacity observed upon use of large sorbent particles was not proportional to the variation in external surface area. Desorption studies were conducted to elucidate the mechanism and recovery of the adsorbate and adsorbent. As the pH of the system increases, the number of negatively charge sites increased. A negatively charged surface site on the adsorbent favors the adsorption of dye electrostatic repulsion. The data reported here should be useful for the design and fabrication of an economically viable treatment process using batch (or) stirred tank reactors for dye adsorption and for diluting industrial effluents.

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