IJST EXPLORE International Journal of Science and Technology
CENTRE OF PROFESSIONAL RESEARCH PUBLICATIONS
ISSN 2049-7318

International Journal of Science and Technology Volume 2 No. 4, April, 2013

Dye Removal from Colored Textile Wastewater Using Synthesized Chitosan

Angham G. Hadi
Babylon University, College of Science, Chemistry Department. Iraq

ABSTRACT

In this research work natural bio polymer "chitosan" was synthesized using fish shells and adsorption of methyl orange (MO; a typical, stable, azo dye) from aqueous solutions was studied. The effects of operational parameters such as chitosan dosage, initial dye concentration, time and pH on dye removal were studied. Results indicated that chitosan could be used as a biosorbent to remove the azo dyes from contaminated water. Synthesize of chitosan involved four main stages as preconditioning, demineralization, deproteinization, decolorization and deacetylation. Chitosan was characterized using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid.

Keywords: *Adsorption; Methyl orange; Chitosan,synthesized.*

1. INTRODUCTION

Dyes are generally present in the effluents of textiles, leather, food processing substances, and paper. about 50% of which are azo dyes [1]. Azo dyes exhibit widely different chemical structures, primarily based on substituted aromatic and N═N groups. Adsorption methods are relatively simple, easy to operate and handle, and cost-effective. Many efforts have been made to remove dyes using low-cost adsorbents, such as sawdust, wheat shell [2], feather [3], clay [4] and [5], peat[6] , and other waste materials [7]. Recently, adsorbents have been developed from naturally occurring materials. These adsorbents have become a focus of environmental investigations because of their low cost and biodegradability [8]. Chitosan (CS), the second most abundant biopolymer in nature after cellulose, has attracted great attention due to its low cost, good film-forming ability, and non-toxicity. In aqueous solutions, amine ($–NH_2$) groups of CS are much easier to cationize, and they strongly adsorb all kinds of dye anions by electrostatic attraction. Today, there is a growing interest in developing natural low-cost alternatives to synthetic polymers [9]. Chitin, found in the exoskeleton of crustaceans, the cuticles of insects and the cells walls of fungi, is the most abundant amino polysaccharide in nature [10], [11] and [12]. This low-cost material is a linear homopolymer composed of β (1-4)-linked *N*-acetyl glucosamine (Figure.1). It is structurally similar to cellulose, but it is an amino polymer and has acetamide groups at the C-2 positions in place of the hydroxyl groups. The presence of these groups is highly advantageous in providing distinctive adsorption functions and conducting modification reactions.

2. MATERIALS AND METHODS

2.1 Preparation of Sorbent

Traditional isolation of chitin consists of four traditional steps (Figure 2): demineralization (DM), deproteinization (DP), decolorization (DC), and deacetylation (DA).

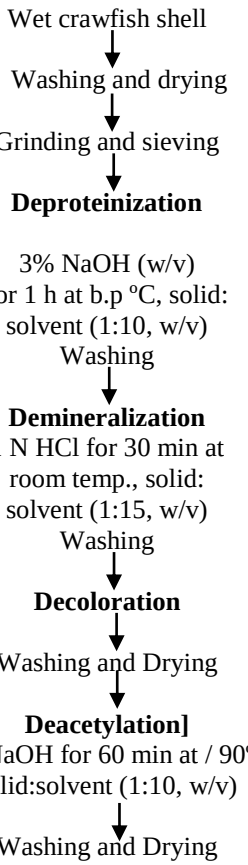

Figure 2. Traditional Chitosan Production [14].

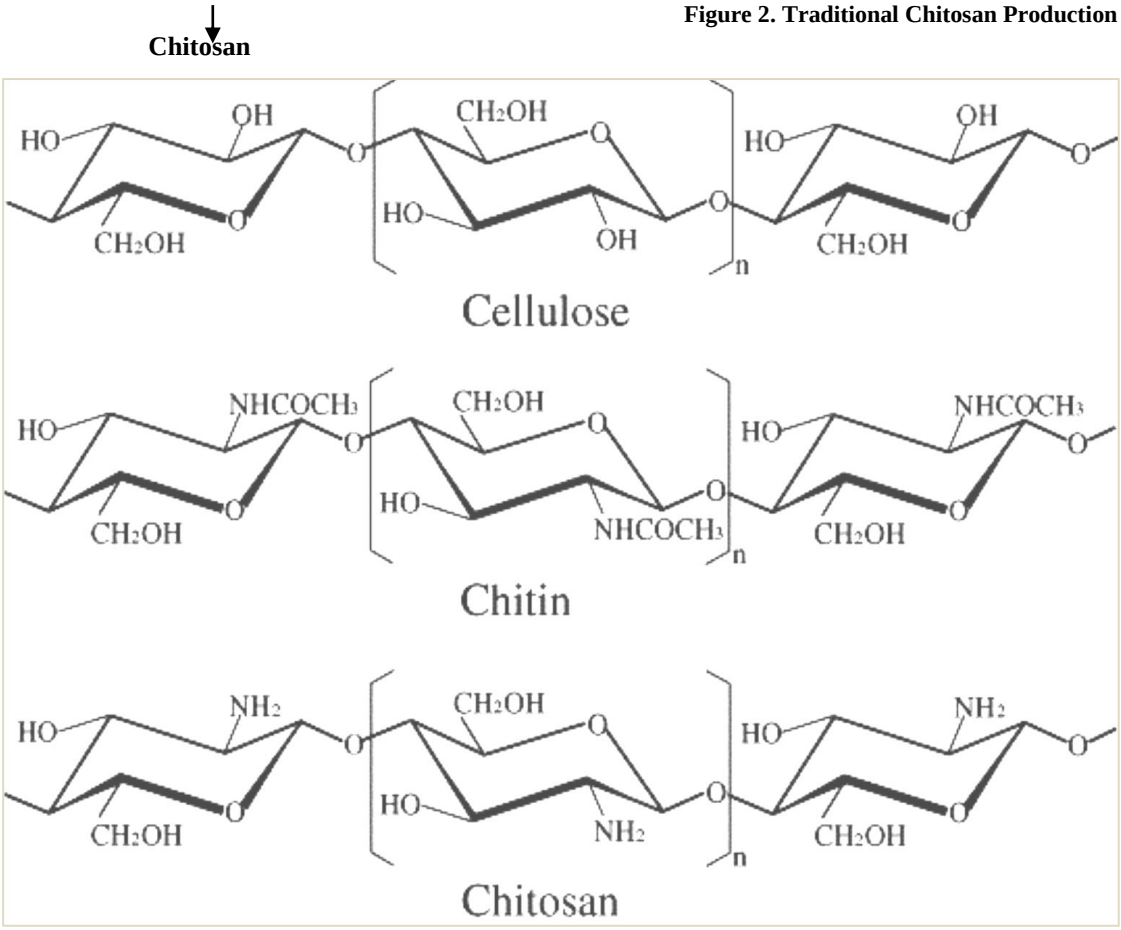

Figure 1. Chemical structures of chitin, chitosan and cellulose [13]

2.2 Batch Adsorption Experiments

A stock solution of MO (1.0 g/L) was prepared by dissolving 1 g of MO powder in 1 L of double distilled water. The desired concentrations ranging from 10 to 60 mg/L were obtained by dilution. For each adsorption experiment, 50 mL of the dye solution with a specified concentration was stirred at 100 rpm in a glass flask. The pH of solutions was adjusted to a desired value by adding 0.1 mol/L NaOH or HCl solution. Batch adsorption experiments were carried out using a thermostated shaker for a certain contact time at a determined temperature at 100 rpm. At predetermined time intervals, samples were withdrawn by a pipette and centrifuged at 4000 rpm. Then, the residual concentration was determined from a constructed calibration curve by measuring the absorbance at λ_{max} = 464.9 nm using UV-Vis spectrophotometer.

Batch adsorption experiments were carried out to examine effects of adsorbent dosage, initial dye concentration, solution pH, and time on the adsorption of MO on chitosan.

The amount of MO adsorbed on chitosan (at a predetermined time *t*), *qt* (in mg/g), was determined using the mass balance equation:

$$qt = (C_{\circ} - Ct) * m / v \quad (1)$$

The decolorization rate (η) of MO was calculated by the following equation:

$$\mu = (C_{\circ} - Ct) / C_{\circ} * 100\% \quad (2)$$

where C_0 is the initial concentration of MO (in mg/L), *Ct* (in mg/L) is the instant concentration of MO at a predetermined time *t*, *V* is the volume of the solution (in L), and *m* is the mass chitosan (in g).

3. RESULTS AND DISCUSSION

3.1 Effect of Adsorbent Dosage

The effect of adsorbent dosage (varied from 0.025 to 0.25 gm) on the percentage removal of 50 mg/L MO

solution is shown in Fig. 3. The percentage removal of MO from the solution increased from 30% to 86% as the adsorbent dosage increased from 0.025 to 0.25 gm. This result is expected because of the increased adsorbent surface area and availability of more adsorption sites caused by increasing adsorbent dosage [15], [16].

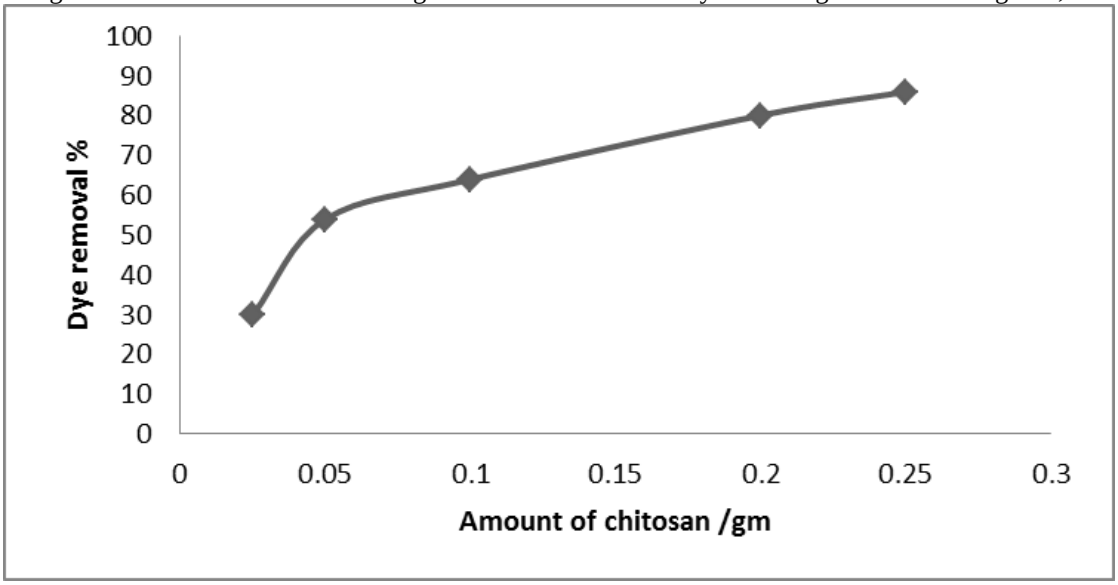

Figure 3. Effect of adsorbent dosage in MO removal

3.2 Effect of Solution pH

The pH of the dye solution affects the surface charge of the adsorbent, the degree of ionization of the materials, and the dissociation of functional groups on the active sites of the adsorbent. As well, it affects the structure of the dye molecule [17]. The percentage removal of MO at different pH values is plotted in Fig. 4. The percentage removal increased from 24.29% to 80.85% when pH was decreased from 10 to 2. This was because the MO molecule (with one sulfuric group) ionized easily even in acidic media and became a soluble MO anion. As the initial solution pH decreased, the number of positively charged active sites increased due to the protonation of the amine groups ($-NH_2$) in the CS chain. Consequently, the electrostatic interaction between the positively charged adsorbent and the MO anions increased, which resulted in increased adsorption. Furthermore, the lower adsorption removal percentage at alkaline pH contributed to the presence of excess hydroxyl ions, which competed with the MO molecules for adsorption sites [16]. In contrast, as expressed in equilibrium equation (3), the quinoid structure of MO is more easily reduced than its azo structure [18]. Therefore, higher removal percentages were observed at acidic pH values for MO adsorption.

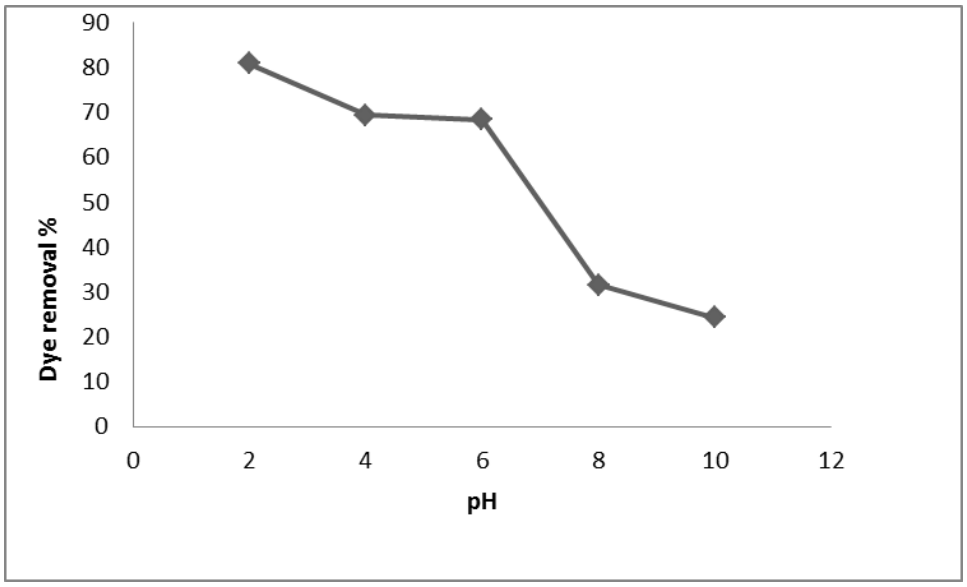

Figure 4. Adsorption of MO by chitosan as a function of pH at initial concentration of 50mg/L and adsorbent dosage 0.1 g.

3.3 Effect of Contact Time

A 50ml of 50mg/L of MO dye was taken in conical flasks and treated with 0.1 gm chitosan (adsorbent) at several times (20, 40, 60, 80, 100, 120 and 140 min.). the variation in percent removal of dye with the time was shown in figure 5. The percentage removal increased from 31.41% to 80.60% when time was increased from 20 to 140 min., this due to saturation of active sites which do not allow further adsorption to take place [19].

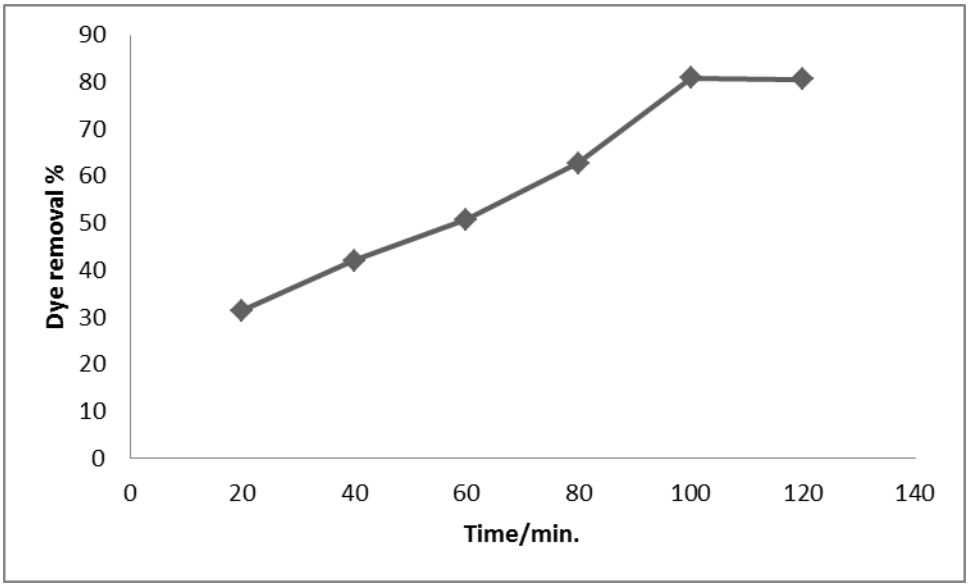

Figure 5. Effect of contact time on MO adsorption(50mg/L) by 0.1gm chitosan.

3.4 Effect of Initial MO Concentration

The effect of initial MO concentration on the percentage removal of the dye is shown in figure 6. The initial MO concentration was varied from 10 to 60 mg/L. A rapid initial adsorption of MO took place within the first 20 min, after which the adsorption slowed down and then almost reached equilibrium at 120 min. The percentage of MO removal evidently decreased with increasing initial dye concentration. The percentage removal was 82.05% for 10 mg/L initial concentration, and only 30.26% for 60 mg/L after 120 min of adsorption (figure 6). This was caused by an increase in the mass gradient pressure between the solution and adsorbent. The gradient acted as

the force that drove the transfer of the dye molecules from the bulk solution to the particle surface [16] and [20].

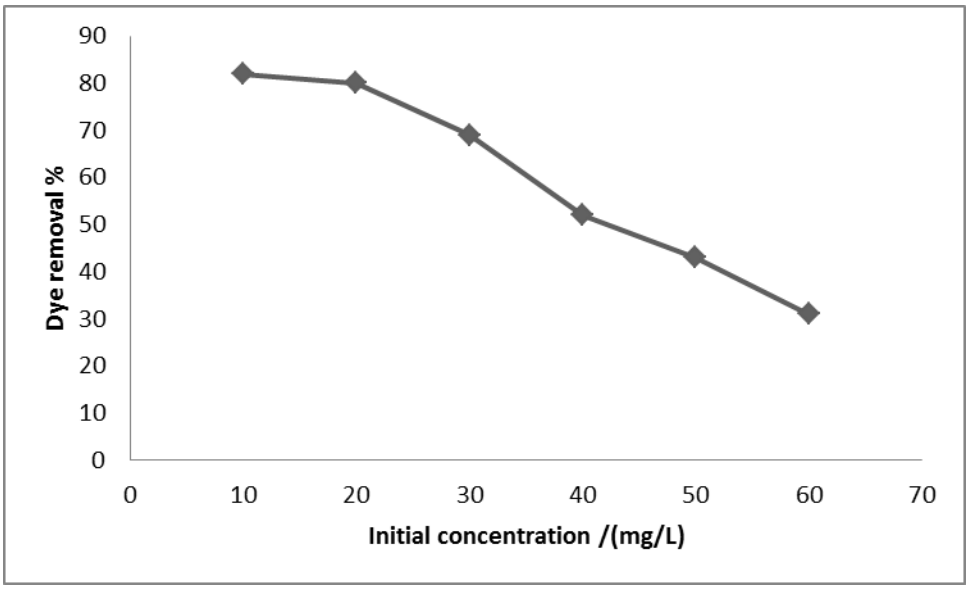

Figure 6. Effect of different initial MO concentration on dye removal

4. CONCLUSION

The synthesize of chitosan involved four main stages as preconditioning, demineralization, deproteinization, decolorization and deacetylation., and characterized by using Fourier Transform Infrared Spectroscopy (FTIR) and solubility in 1% acetic acid. MO adsorption onto the chitosan depended highly on adsorbent dosage, initial dye concentration, solution pH and time.

REFERENCES

[1] Q.Y. Sun, L.Z. Yang, The adsorption of basic dyes from aqueous solution on modified peat-resin particle , Water Res., 37 (7) (2003), pp. 1535–1544.

[2] A. Mittal, A. Malviya, D. Kaur, J. Mittal, L. Kurup, Studies on the adsorption kinetics and isotherms for the removal and recovery of methyl orange from wastewaters using waste materials, J. Hazard. Mater., 148 (1–2) (2007), pp. 229–240.

[3] A.R. Cestari, E.F.S. Vieira, A.A. Pinto, E.C.N. Lopes,Multistep adsorption of anionic dyes on silica/chitosan hybrid. 1. Comparative kinetic data from liquid- and solid-phase models J. Colloid Interface Sci., 292 (2) (2005), pp. 363–372.

[4] Y.L. Liu, Y.H. Su, J.Y. Lai,In situ crosslinking of chitosan and formation of chitosan–silica hybrid membranes with using γ-glycidoxypropyl trimethoxysilane as a crosslinking agent,Polymer, 45 (2004), pp. 6831–6837.

[5] J. Wang, P.V.A. Pamidi, D.S. Park,Screen-printable sol–gel enzyme-containing carbon inks,Anal. Chem., 68 (1996), pp. 2705–2708.

[6] Q.H. Shi, Y. Tian, X.Y. Dong, S. Bai, Y. Sun,Chitosan-coated silica beads as immobilized metal affinity support for protein adsorption,Biochem. Eng. J., 16 (2003), pp. 317–322.

[7] J.M. Wu, M.M. Luan, J.Y. Zhao,Trypsin immobilization by direct adsorption on metal ion chelated macroporous chitosan–silica gel beads, orange from wastewaters using waste materials,J. Hazard. Mater., 148 (1–2) (2007), pp. 229–240.

[8] M.P. Elizalde-González,Development of non-carbonized natural adsorbents for removal of textile dyes,Trends Chem. Eng., 10 (2006), pp. 55–66.

[9] G. Crini,Non-conventional low-cost adsorbents for dye removal: a review, Bioresour. Technol., 60 (2006), pp. 67–75.

[10] J. Synowiecki, N.A. Al-Khateeb, Production, properties, and some new applications of chitin and its derivatives, Crit. Rev. Food Sci. Nutr., 43 (2003), pp. 145–171.

[11] M.H. Struszczyk, Chitin and chitosan—part I. Properties and production, Polimery, 47 (2002), pp. 316–325.

[12] M. Rinaudo,Chitin and chitosan: properties and applications, Prog. Polym. Sci., 31 (2006), pp. 603–632.

[13] WEB_4,2007.Dalwoo-ChitosanCorporation, http;// members.tripod.com/Dalwoo/structure.

[14] Meyers, S.P. and No, H.K. 1995. Utilization of crawfish pigment and other fishery processing by-products. Ch. 20. In "*Nutrition and Utilization Technology in Aquaculture*," Lim, C.E and Sessa, D.J. (Eds.), p. 269-277. AOCS Press, Champaign, IL.

[15] L. Wang, J. Zhang, R. Zhao, C. Li, Y. Li, C.L. Zhang,Adsorption of basic dyes on activated carbon prepared from Polygonum orientale Linn: equilibrium, kinetic and thermodynamic studies, Desalination, 254 (1–3) (2010), pp. 68–74.

[16] P.S. Kumar, S. Ramalingam, C. Senthamarai, M. Niranjanaa, P. Vijayalakshmi, S. Sivanesan, Adsorption of dye from aqueous solution by cashew nut shell: studies on equilibrium isotherm, kinetics and thermodynamics of interactions, Desalination, 261 (1–2) (2010), pp. 52–60.

[17] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, Sep. Purif. Technol., 53 (1) (2007), pp. 97–110.

[18] V.F. Chemie, New methods for determination of β-lactam antibiotics by means of diffuse reflectance spectroscopy using polyurethane foam as sorbent, PhD thesis. Duisburg University, Germany, 2005.

[19] W. Nakbanpote,P. Thiravavetyan and C. Kalambaheti,Mineral Eng.,13,391-552(2002).

[20] D.S. Bhargava, S.B. Sheldarkar, Use of TNSAC in phosphate adsorption studies and relationships. Effects of adsorption operating variables and related relationships, Water Res., 27 (2) (1993), pp. 313–324.