Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2014.950990

56 (2015) 1458–1464
November

Taylor & Francis
Taylor & Francis Group

Treatment of textile mill effluent using low molecular weight crab shell chitosan

M. Geetha Devi[a,*], Rahma Salim Al-kindi[a], G. Chandrasekar[b], Murtuza Ali Syed[a], S. Feroz[c]

[a]*Department of Mechanical and Industrial Engineering, Caledonian College of Engineering, P.O. Box 2322, Al-Hail, Muscat, PC 111, Oman, Fax: +00968 24536165; emails: gdmdevi@gmail.com (M.G. Devi), r.s.kindi12@gmail.com (R.S. Al-kindi), smurtuzaali@gmail.com, murtuza@caledonian.edu.om (M.A. Syed)*
[b]*Department of Chemical Engineering, Pondicherry Engineering College, Pondicherry, India, Fax: +00914132655281; email: chandrasekar@pec.edu (G. Chandrasekar)*
[c]*CCCI Department, Caledonian College of Engineering, P.O. Box 2322, Al-Hail, Muscat, PC 111, Oman, Fax: +00968 24536165; email: feroz2005@gmail.com (S. Feroz)*

Received 10 January 2014; Accepted 11 July 2014

ABSTRACT

Inexpensive and eco-friendly biosorbent crab shell chitosan has been successfully used for the treatment of textile mill effluent. The present study investigated the application of low molecular weight (20 kDa) crab shell chitosan in the treatment of textile industry effluent in a most efficient and economical way. A series of batch experiments were conducted by varying solution pH, agitation time, chitosan dosage, and agitation speed. The parameters considered for the study are chemical oxygen demand (COD), total suspended solids (TSS), total dissolved solids (TDS), and turbidity. The observed experimental result showed that low molecular weight crab shell chitosan could able to reduce significantly the COD, TSS, TDS, and turbidity from textile mill effluent. The optimum conditions were obtained at 150 mg/L of chitosan dosage, pH 4, 4 h of mixing time, and a mixing speed of 75 RPM. The results show that low molecular weight crab shell chitosan can be used for the effective treatment of textile mill effluent.

Keywords: Adsorption; Biopolymers; Chemical oxygen demand; Crab shell chitosan; Effluent treatment; Textile mill effluent

1. Introduction

Increasing public awareness and stringent environmental regulations has led to a new search for environmental friendly and inexpensive methods to treat industrial effluent. Textile industry is one of the rapidly growing industries, and it has a high importance in terms of its environmental impact, since it consumes considerably high amounts of freshwater and discharges almost same quantity of wastewater. The treatment of textile industry wastewater by economical means is a real challenge to researchers and scientists. The contaminants present in the textile industry wastewater are organics, color, toxic materials, salt, chlorine compounds, and inhibitor compounds [1]. Commonly employed techniques for the removal of dye from wastewater are adsorption,

*Corresponding author.

Table 1
Typical composition of textile mill wastewater

	Range of values
pH	7–9
Biochemical oxygen demand (mg/L)	80–6,000
Chemical oxygen demand (mg/L)	150–12,000
Total suspended solids (mg/L)	15–8,000
Total dissolved solids (mg/L)	2,900 −3,100
Chloride (mg/L)	1,000–1,600
Total Kjeldahl nitrogen (mg/L)	70–80
Color (Pt-Co)	50–2,500

coagulation, flocculation, electrochemical process, etc. [2,3]. Traditional wastewater technology includes physical, chemical, and biological treatment methods etc. It has been reported that conventional biological treatment processes are not suitable due to low degradation rate of the dye chemicals. The disadvantage of chemical method is the accumulation of large quantity of sludge that could create disposal problem [4,5] and also require large amount of electrical energy which further possess environmental problem [6–8]. Among these methods, adsorption technique is superior due to simplicity in operation and easy handling. A variety of adsorbents [9–12] have been employed for the treatment of textile wastewater. The typical composition of textile industry wastewater is shown in Table 1 [13–25].

The possibility of using low-cost materials such as guava seed [26], bituminous coal [27], olive waste [28], waste biomass [29,30] in the treatment of textile industry wastewater has been studied.

The objective of the present study was to explore the feasibility of using low molecular weight crab shell chitosan in the treatment of textile industry effluent. The attractive features of crab shell chitosan are biodegradability, biocompatibility, antibacterial, nontoxic and can be used as coagulant, flocculent for the removal of organics, pathogens, suspended solids, and turbidity [31–34]. Our recent study shows the importance of chitosan in the treatment of wastewater from various industries [35–39]. The main advantage for the use of chitosan as an adsorbent in wastewater treatment is due to its local availability, environmental friendly nature, and cost-effectiveness. No major studies have been carried out for the treatment of textile industry wastewater using low molecular weight crab shell chitosan.

The research was carried out during March 2013, and the effluent was collected from a leading textile industry in the sultanate of Oman.

2. Materials and methods

Crab shell chitosan powder of low molecular weight (20 kDa) with 80% degree of deacetylation was purchased from Sigma-Aldrich, Bangalore, India. 1 M HCl/1 M NaOH solutions prepared in pure distilled water of high purity were used for pH adjustment. The chemical structure of low molecular weight crab shell chitosan is shown in Fig. 1.

Chitosan is a linear β-1, 4-linked polysaccharide, obtained by the partial deacetylation of chitin. The functional properties of chitosan were explained elsewhere [40–44].

The investigations were carried out with the textile mill effluent before and after treatment. The wastewater samples were allowed to settle before characterization. The samples were preserved at 4˚C in order to avoid any bacterial contamination. To ensure the accuracy, reliability, and reproducibility of the collected data, all batch experiments were carried out in triplicate and the mean values of three data sets are presented.

The parameters considered in the study are COD, TDS, TSS, and turbidity. COD measurements were performed by calorimetric method using spectrophotometer (AQ 400, Thermo Scientific Orion and Thermo Reactor Orion COD 125), surface morphology study by scanning electron microscope (JSM-840A), and turbidity by turbidity meter (WTW Turb 550). Surface characterization of the chitosan powder was performed using scanning electron microscope (SEM) to visualize the quality and morphology of the adsorbent before and after treatment.

All batch experiments were conducted at room temperature (25 ± 2˚C) by mixing required amount of chitosan powder with 500 mL of textile mill effluent and kept under stirring. Samples were collected at fixed time intervals and allowed to settle before characterization. To maximize the pollution removal efficiency, batch experiments were conducted at ambient temperature using optimum conditions of all pertinent parameters. For COD measurement, the sample was reacted with an acidic solution of potassium

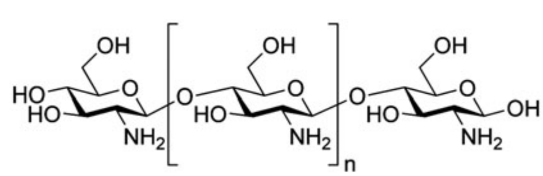

Fig. 1. Chemical structure of low molecular weight crab shell chitosan.

dichromate in the presence of a catalyst (silver) and digested for 2 h at a temperature of 150°C.

The percentage removal efficiency was calculated by Eq. 1

$$\%\,\text{removal efficiency} = \frac{C_0 - C_1}{C_0} \times 100 \quad (1)$$

where C_0 and C_1 are the initial and final concentrations in mg/L, respectively.

COD, TSS, TDS, and turbidity of the samples before and after treatment were analyzed according to standard methods [45].

3. Results and discussion

3.1. Effect of pH

The effect in variation of solution pH was studied by altering the effluent solution pH from 3 to 10. The experimental results are shown in Fig. 2. It has been observed that the dye adsorption efficiency decreased with increase in solution pH. The main interaction between chitosan and dye molecule are electrostatic in nature. At low pH, the surface charge of chitosan becomes full, which leads to strong electrostatic attraction between the adsorbent surface and anionic dye molecule that results in increased adsorption rate.

The optimum pH for the effective removal of COD was found to be 4, and above which, the COD removal is not attractive. This decrease in efficiency is due to the weak interaction between the amino groups present in chitosan surface and oppositely charged ions present in the wastewater. At higher pH, the surface charge of chitosan will disappear and become deprotonated. In acidic conditions, chitosan would behave like a polyelectrolyte. The protonation of amino groups in chitosan leads to positive charge and hence, the electrostatic interaction will be strong. Chitosan is a very attractive polymer by allowing the molecules to bind negatively charged particles via ionic or hydrogen bonding or electrostatic interaction. This will further reduce or neutralize the particles surface charge. So pH has a major role in the parameter reductions. It is observed that maximum percentage reduction was reached at pH 4. Chitosan recorded the highest percentage reduction in COD (71%) at pH 4, and beyond this pH, it showed a decreasing trend in the removal efficiencies, as illustrated in Fig. 2. This could be due to the surface charge reversal as well as destabilization of polymer bridging.

The active sites on the surface of chitosan are positively charged at acidic pH and will adsorb oppositely charged ions present in the effluent. At basic pH, there are no exchangeable ions on the surface of chitosan, which causes repulsion between the molecules and hence less adsorption rate. Fifty percent turbidity reduction was observed at pH 4. The destabilization of particles becomes less important due to less positive surface charge of chitosan at low pH. The maximum percentage reduction in TSS was obtained at pH 6, whereas the maximum percentage reduction in TDS occurred at pH 4.

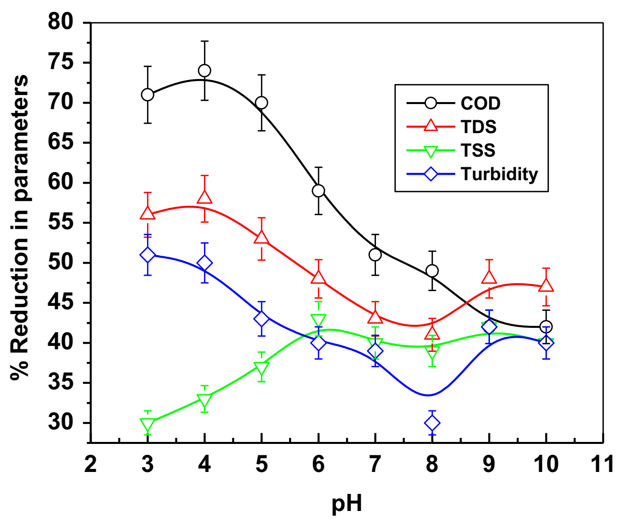

Fig. 2. Effect of pH on the percentage reduction of parameters. Conditions: adsorbent dose: 150 mg/L, volume of sample: 500 mL, temp: 25°C, initial adsorbate conc: 10 mg/L, time of contact: 4 h.

3.2. Effect of stirring time

Mixing time plays an important role in the parameter reductions. An optimum contact time to achieve effective removal of pollutants was investigated. It was found that the removal efficiency increased with increase in contact time up to 4 h. Further increase in stirring time results decrease in efficiency. Typically, 78% of the COD reduction was achieved in the first 4 h followed by a decrease in efficiency with an initial concentration of 150 mg/L and an adsorbent dosage of 10 mg/L.

The adsorption phenomena started immediately after the addition of chitosan. It was observed that a contact time of 4 h could give maximum percentage reduction in COD and TDS, whereas the maximum percentage reduction in TSS and turbidity was attained at 8 h. At low mixing time, the collision between the particles and chitosan surface are low, which results in low adsorption rate. The results are shown in Fig. 3. The percentage reduction in TSS was

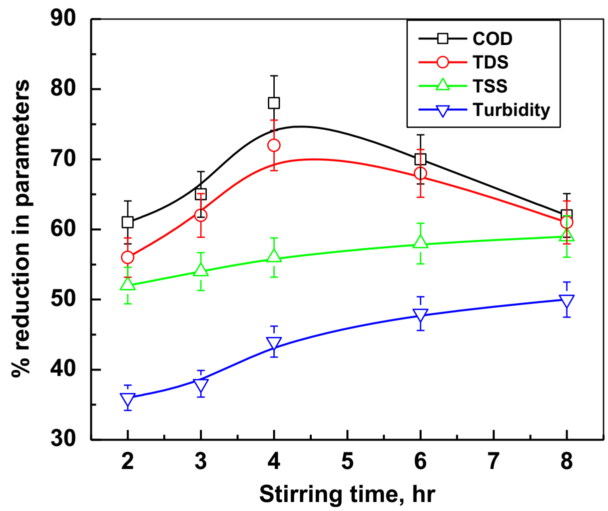

Fig. 3. Effect of stirring time. Conditions: adsorbent dose: 150 mg/L, volume of sample: 500 mL, temp: 25℃, initial adsorbate conc: 10 mg/L, pH = 4.

least at 2 h. A significant improvement in residual water turbidity was observed with increased mixing times. For further optimization of other parameters, this contact time was considered as the optimum time.

3.3. Effect of dosage of chitosan

The effect of dosage of chitosan was studied by varying the amounts of adsorbent from 50 to 300 mg/L, while keeping other parameters (pH 4, agitation speed 50 RPM, and mixing time 4 h) constant. The results are presented in Fig. 4, which showed the effect of dosage of chitosan on various parameter reductions. The percentage reduction in COD increased with increase in chitosan dosage up to 150 mg/L, and above which, there was no significant change in COD reduction. This phenomenon could be explained based on the charge density. This is expected to be the higher dosage of adsorbent will increase the surface area and greater will be the availability of exchangeable sites for the ions. Referring to the Fig. 4, the maximum reduction in COD was 80% at a dosage of 150 mg, but the maximum percentage reduction in TSS was reached at 50 mg chitosan dosage. This may be due to the fact that overdosage of chitosan will lower the percent reduction in TSS. Higher amount of chitosan was required to achieve the best result, since chitosan has a high charge density and adsorption increased as the charge density of the polymer increased. This may be due to the fact that overdosing produces restabilized particles, due to unavailable site for the formation of bridges, resulting in steric repulsion. The excess dosage has the possibility to get a charge reversal, which led to particle restabilization. For the optimum adsorbent dosage of 150 mg, chitosan recorded the highest reduction in parameters, which were 80% both in COD and turbidity reduction, respectively. The percentage reduction in TSS shows a decreasing trend.

3.4. Effect of stirring speed

The effect of stirring speed was studied by varying the speed between 25 to 150 RPM at constant

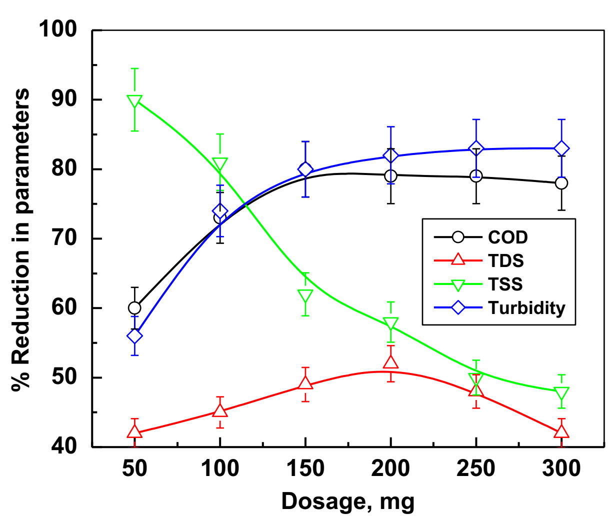

Fig. 4. Effect of dosage of adsorbent on the removal of parameters. Temp: 25℃, volume of sample: 500 mL, absorbent dose: 150 g/L, contact time: 4 h, pH: 4.

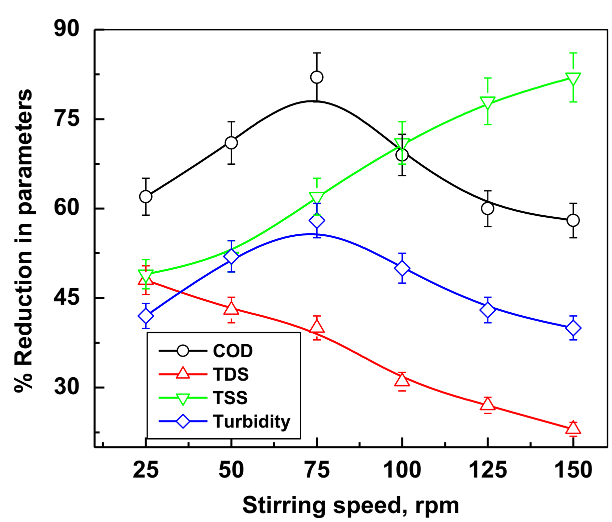

Fig. 5. Effect of speed Temp: 25℃, absorbent size: mixed, volume of sample: 500 mL, absorbent dose: 150 g/L, contact time: 4 h, pH: 4.

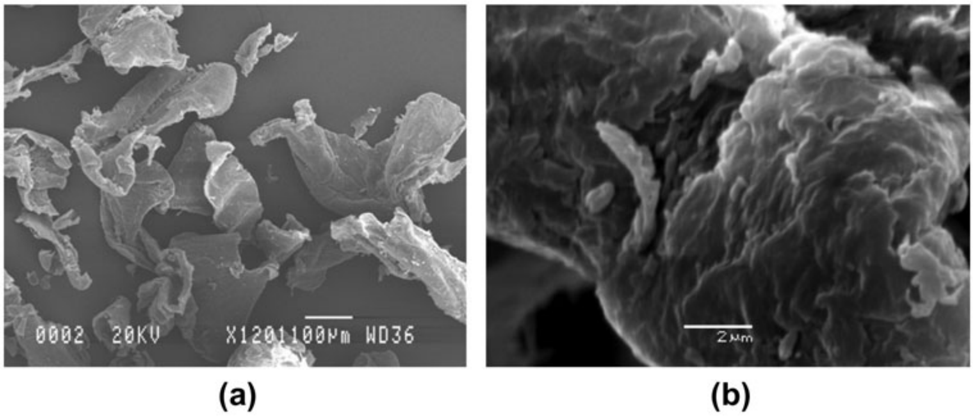

Fig. 6. SEM of chitosan before treatment at a magnification of 1201X (a) and after (b) treatment at a magnification of 1201X.

concentration and stirring time of 4 h. It was observed that when the mixing speed was increased to more than 75 RPM, the percentage reduction was lowered. This is due to the breakdown of particles and dispersed again in the sample.

For an RPM of 75, the adsorption was reached at its maximum. This may be due the attractive force between chitosan and ions present in the solution. When speed is increased to 150 RPM, the percentage reductions in parameters were low. That is at higher RPM, the percentage reduction in COD was not satisfactory due to breakdown of the expanding chains and flocs. The results indicate that there is a decrease in the extent of adsorption with increase in speed of agitation. The results are shown in Fig. 5.

Fig. 6(a) and (b) shows the surface morphology of the adsorbent before and after treatment. It is seen that the SEM image of chitosan powder before treatment showed clear, scattered, and evenly distributed morphology, whereas after treatment image showed clustered and thick structure (Fig.6(b)), which indicates most of the contaminants present in the effluent are adsorbed onto chitosan powder. This shows the effective removal of pollutants from the effluent.

3.5. Adsorption isotherm and kinetics studies

Adsorption kinetics was studied using chitosan, and the results are presented in Fig. 7, which showed a linear trend with R^2 value greater than 0.98. Based on the data from adsorption experiments, Langmuir isotherm was obtained for the treated effluent as shown in Fig. 8, which suggests that adsorption capacity of chitosan is significant.

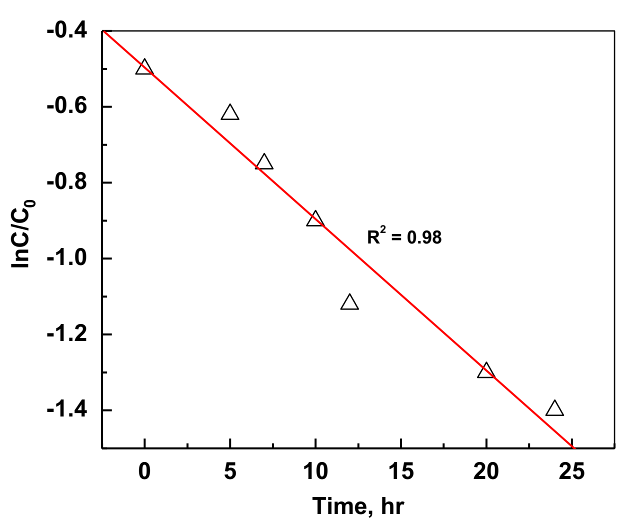

Fig. 7. Adsorption kinetics.

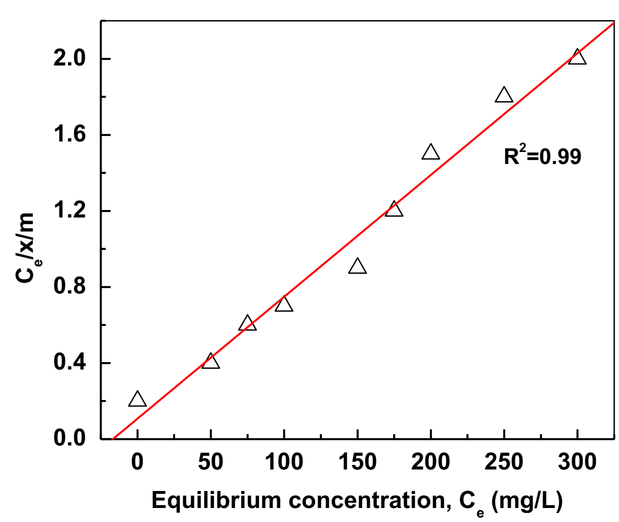

Fig. 8. Langmuir Isotherm.

4. Conclusion

The experimental investigation on the possible use of low molecular weight crab shell chitosan in the treatment of textile mill effluent revealed that the pollutants present in the textile mill effluent are successfully removed in an efficient and environmental friendly manner. It was observed that the removal efficiency of adsorbent was optimum at a pH of 4. Also, chitosan can be employed as a very good adsorbent due to its ability in treating the textile industry effluent in a most economical way and found minimal adsorbent dosage requirement in treatment processes. Chitosan is a cheap and environmental friendly biopolymer derived from crab shell. Further, current study may also be helpful to adopt the crab shell chitosan as an adsorbent in continuous processes; however, there is a need to do column studies to prove this aspect. Currently, we are investigating the performance of chitosan in column studies for the regeneration of adsorbent.

References

[1] S. Sandhya, K. Swaminathan, Kinetic analysis of treatment of textile wastewater in hybrid column up flow anaerobic fixed bed reactor, Chem. Eng. J. 122 (2006) 87–92.

[2] J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong, Treatment of dye aqueous solutions using Nano filtration polyamide composite membrane for the dye wastewater reuse, Dyes Pigm. 76 (2008) 429–434.

[3] R. Malik, D.S. Ramteke, S.R. Wate, Adsorption of malachite green on groundnut shell waste based powdered activated carbon, Waste Manage. 27 (1999) 57–71.

[4] C.H. Weng, Y.C. Sharma, S.H. Chu, Adsorption of Cr(VI) from aqueous solutions by spent activated clay, J. Hazard. Mater. 155 (2008) 65–75.

[5] Y.C. Sharma, Uma, S.N. Singh, F. Gode, Fly ash for the removal of Mn(II) from aqueous solutions and wastewaters, Chem. Eng. J. 132 (2007) 319–323.

[6] M. Matto, Q. Hussain, Decolourization of direct dyes by salt fractionated turnip proteins enhanced in the presence of hydrogen peroxide and redox mediators, Chemosphere 69 (2007) 338–345.

[7] M. Ahmedna, W.E. Marshall, R.M. Rao, Production of granular activated carbons from selected agricultural by-product and evaluation of their physical, chemical and adsorption properties, Bioresour. Technol. 71 (2000) 113–123.

[8] D. Pak, W. Chang, Decolourizing dye wastewater with low temperature catalytic oxidation, Water Sci. Tech. 40 (1999) 115–121.

[9] M. Alkan, S. Celikcapa, O. Demirbas, M. Dogan, Removal of reactive blue 221 and acid blue 62 anionic dye from aqueous solutions by sepiolite, Dyes Pigm. 65 (2005) 251–259.

[10] C.C. Wang, L.C. Juang, T.C. Hsu, C.K. Lee, J.F. Lee, F.C. Huang, Adsorption of basic dyes onto montomorillonite, J. Colloid Interface Sci. 273 (2004) 80–86.

[11] A.G. Espantaleón, J.A. Nieto, M. Fernantez, A. Marsal, Use of activated clays in the removal of dyes and surfactants from tannery waste waters. Applied Clay Science 24 (2003) 105–110.

[12] A. Gurses Karaca, S. Dogar, C. Acikyildiz, M. Yalcin, Determination of adsorptive properties of clay/Water system: Methylene blue sorption, J. Colloid Interface Sci. 269 (2004) 310–314.

[13] H.L. Sheng, M.L. Chi, Treatment of textile waste effluents by ozonation and chemical coagulation, Water Res. 27 (1993) 1743–1748.

[14] M. Tzitzi, D.V. Vayenas, G. Lyberatos, Pretreatment of textile industry wastewaters with ozone, Watar Sci and Tech. 29 (1994) 151–160.

[15] M.C. Venceslau, S. Tom, J.J. Simon, Characterization of textile wastewaters—A review, Environ. Tech. 15 (1994) 917–929.

[16] U. Altinbas, S. Domeci, A. Baristiran, Treatability study of wastewater from textile industry, Environ. Tech. 16 (1995) 389–394.

[17] T. Olcay, K. Isik, E. Gülen, O. Derin, Color removal from textile wastewaters, Water Sci. Tech. 34 (1996) 9–11.

[18] L. StanisŁaw, G. Monika, Optimization of oxidants dose for combined chemical and biological treatment of textile wastewater, Water Res. 33 (1999) 2511–2516.

[19] C. Gianluca, R. Nicola, Technical note, the treatment and reuse of wastewater in the textile industry means of ozonation and electroflocculation, Water Res. 35 (2001) 567–572.

[20] I.A. Arslan, A.B. Isil, The effect of pre-ozonation on the H_2O_2/UV–C treatment of raw and biologically pre-treated textile industry wastewater, Water Sci. Tech. 45 (2002) 297–304.

[21] P.G. Melidis, A. Aivasidis, K. Gimouhopoulos, Degradation of azo-reactive dyesby ultraviolet radiation in the presence of hydrogen peroxide, Dyes Pigm. 52 (2002) 69–78.

[22] F.S. Mehmet, Z.S. Hasan, Ozone treatment of textile effluents and dyes: Effect of applied ozone dose, pH and dye concentration, J. Chem. Tech. Biotech. 77 (2002) 842–850.

[23] B. Ahmet, Y. Ayfer, L. Doris, N. Nese, K. Antonius, Ozonation of high strength segregated effluents from a woollen textile dyeing and finishing plant, Dyes Pigm. 58 (2003) 93–98.

[24] Metcalf Eddy, Inc., Wastewater Engineering Treatment and Reuse, fourth Edition, McGraw-Hill, New York, NY, 2003.

[25] N. Azbar, T. Yonar, K. Kestioglu, Comparison of various advanced oxidation processes and chemical treatment methods for COD and colour removal from a polyester and acetate fiber dying effluent, Chemosphere 55 (2004) 35–43.

[26] C.G. Joseph, A.B. Krishnaiah, K.O. Soon, Sorption studies of methylene blue dye in aqueous solution by optimized carbon prepared from Guava seeds (*Psidium guajava* L), Mater. Sci. 13 (2007) 83–87.

[27] D. Cuhadaroglu, O.A. Uygun, Production and characterization of activated carbon from a bituminous coal by chemical activation, Afr. J. Biotechnol. 7 (2008) 3703–3710.

[28] R. Baccar, J. Bouzid, M. Feki, A. Montiel, Preparation of activated carbon from Tunisian olive waste cakes. J. Hazard. Mater. 162 (2009) 1522–1529.

[29] A.A. Nunes, A.S. Franca, L.S. Oliveira, activated carbon from waste biomass: An alternative use for biodiesel production solid residues, Bioresour. Technol. 100 (2009) 1786–1792.
[30] Y.C. Chung, Y.H. Li, C.C. Chen, Pollutant removal from aquaculture wastewater using the biopolymer chitosan at different molecular weights, J. Environ. Sci. Health. Part A 40 (2005) 1775–1790.
[31] Y.C. Chung, Improvement of aquaculture wastewater using chitosan of different degrees of deacetylation, Environ. Technol. 27 (2006) 1199–1208.
[32] N.V.R.K. Majeti, A review of chitin and chitosan applications, React. Funct. Polym. 46 (2000) 1–27.
[33] C.W. Feng, L.T. Rud, S.J. Ruey, Comparative adsorption of metal and dye on flake and bead- types of chitosans prepared from fishery wastes, J. Hazard. Mater. 73 (2000) 63–75.
[34] M.G. Devi, Z.S.S. Al-Hashmi, G.C. Sekhar, Treatment of vegetable oil mill effluent using crab shell chitosan as adsorbent, Int. J. Environ. Sci. Technol. 9 (2012) 713–718.
[35] M.G. Devi, J. Joefel, S. Feroz, Dairy wastewater treatment using low molecular weight crab shell chitosan, J. Inst. Eng. India Ser. E. 12 (2012) 108–111.
[36] M.G. Devi, G.C. Sekhar, A batch study on adsorption of zinc (II) using high molecular weight crab shell chitosan and date seed, Int. J. Biotech Chem. Environ. Eng. 1 (2012) 22–26.
[37] M.G. Devi, A.S.A. Khadija, S. Feroz, A.S. Murtuza, Treatment of textile industry effluent using multilayer thin films, Int. J. Eng. Res. Technol. 2 (2013) 22–28.
[38] M.G. Devi, S.S.A. Suhail, S. Feroz, A comparative study on adsorption of chromium (VI) Using high molecular weight crab shell chitosan and date seed carbon, J. Chitin Chitosan Sci. 2 (2013) 1–5.
[39] M. Rinaudo, G. Pavlov, J. Desbrieres, Influence of acetic acid concentration on the solubilization of chitosan. Polymer 4 (1999) 7029–7032.
[40] P. Sorlier, A. Denuziere, C. Viton, A. Domard, Relation between the degree of acetylation and the electrostatic properties of chitin and chitosan, Biomacromolecules 2(3) (2001) 765–772.
[41] S.P. Strand, M.S. Vandvik, K.M. Vårum, K. Østgaard, Screening of chitosan and conditions for bacterial flocculation, Biomacromolecules 2 (2001) 121–133.
[42] M.W. Anthonsen, O. Smidsrod, Hydrogen ion titration of chitosans with varying degrees of N-acetylation by monitoring induced 1H-NMR chemical shifts, Carbohydr. Polym. 26(4) (1995) 303–305.
[43] K.M. Varum, M.H. Ottoy, O. Smidsrod, Water-solubility of partially N-acetylated chitosans as a function of pH: Effect of chemical composition and depolymerization, Carbohydr. Polym. 25 (1994) 65–70.
[44] K. Kurita, T. Sanna, Y. Iwakura, Studies on chitin VI. Binding of metal cations, J. Appl. Polym. Sci. 23 (1979) 511–518.
[45] American Public Health Association (APHA-AW-WAWPCH), Standard Methods for the Examination of Water and Waste Water, Twentieth ed., APHA Washington, DC, 1998, pp. 1270.