Int. J. Environ. Sci. Technol. (2012) 9:713–718
DOI 10.1007/s13762-012-0100-4

ORIGINAL PAPER

Treatment of vegetable oil mill effluent using crab shell chitosan as adsorbent

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Received: 3 May 2011 / Revised: 1 August 2011 / Accepted: 30 December 2011 / Published online: 10 August 2012

Abstract In this study, a naturally available crab shell chitosan of low molecular weight (20 kDa) has been used as adsorbent to evaluate the pollution load in vegetable oil mill effluent. A series of batch experiment was conducted by varying chitosan dosage (100–400 mg), pH (2–9), stirring time (15–90) min and agitation speed (25–150 rpm) to study their effects on adsorption and flocculation processes. The parameters considered for adsorption study are chemical oxygen demand, total suspended solids, electrical conductivity and turbidity. The maximum reduction in chemical oxygen demand, total suspended solids, electrical conductivity and turbidity is 74, 70, 56 and 92 % , respectively. The observed experimental result showed that crab shell chitosan could able to reduce significantly the chemical oxygen demand, turbidity, electrical conductivity and suspended matter. The optimum conditions were estimated as 400 mg/l chitosan, pH 4 and 45 min of mixing time with mixing speed of 50 rpm. Chitosan showed very good pollution removal efficiency and can be used for the effective treatment of vegetable oil mill effluent.

Keywords Adsorption · Biodegradable polymer · Chemical oxygen demand · Effluent treatment · Vegetable oil refinery

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Introduction

Vegetable oil mill effluent treatment is a major issue of environmental concern in developing countries for the last three decades. The waste streams come out from vegetable oil refinery create serious environmental problem such as great threat to aquatic life due to its high organic content. Hence, its treatment is essential prior to its disposal. The choice of effluent treatment method depends on the organic content present in the effluent and its discharge conditions (Chipasa 2001). Many methods were available to treat organic content and a great deal of literature is available on this aspect (Ahmad et al. 2005; Azbar and Yonar 2004; Belli et al. 2004; Bauer et al. 2004; Bux and Mkhize 2001; Chattopadhyay et al. 2003; Bux et al. 2003; Correia et al. 2005; Kale et al. 2002; Kontominas and Taralas 2005). The selection of proper treatment method is crucial in effluent treatment. Some studies suggest physico-chemical and biological treatment methods for the removal of organics from oil mill discharge. However, still there is a waste generated that poses a major challenge in the vegetable oil processing industry (Boyer 1984; Choffel 1976; Seng 1980; Refaat 2010). The presence of volatile acids, alcohols, aldehydes and other suspended matter in vegetable oil mill effluent creates toxicity and reports showed that these toxic ingredients are also related to the low pH (Agha et al. 1998; Bernal et al. 1999). This serious environmental problem can be solved by applying low cost, environmental friendly polymers, such as chitin and chitosan (Crini 2005; Meyers and No 2000).The use of low cost chitin has tried to remove metals, dyes and organic compounds (Guibal 2004; Dempsey et al. 2005, 2006). Recent research on the effective removal of anionic dyes with chitosan has been a great success (Badot and Crini 2008). The degree of deacetylation of chitosan influences the efficiency in removing azo dyes (Ichikawa et al. 2005). The metal adsorption capacity of chitosan affects the distribution of acetyl groups (Iwakura et al. 1979). Another study illustrates the coagulation efficiency of chitosan with respect to the molecular weight (Bough and Landes 1978; Chen et al. 2000).

Considering all these applications, chitosan can be recommended as a good adsorbent because of its excellent properties like biodegradability, biocompatibility, adsorption, antibacterial property and non-toxicity, and can be used as a coagulant, bactericide, pollutant reducing agent for removal of organics, pathogens, suspended solids, turbidity, biological oxygen demand (BOD), chemical oxygen demand (COD), etc. (Chen et al. 2005; Chung 2006; Feng et al. 2000; Majeti 2000). The main advantage for the use of chitosan as an adsorbent in waste water treatment is because of its local availability, environmental friendly nature and cost effectiveness.

Having appropriate treatment processes at right time makes a meaningful difference in operating cost, efficiency and profitability. Hence, in this study, special attention has been given to biopolymers derived from crustacean shells such as crab shell chitosan of low molecular weight (20 kDa), which is environmentally friendly biomaterial and economical.

Low-cost adsorbents with highly efficient adsorption capacities are still under development to reduce pollution load in waste water. Apparently, no major studies have been done to treat vegetable oil mill wastewater using crab shell chitosan. Therefore, this study was carried out to analyze the effect of low molecular weight crab shell chitosan as an adsorbent in the treatment of vegetable oil mill effluent. The optimum pH, dosage, speed and mixing time needed to achieve the best performance of chitosan were determined.

The research was carried out in Muscat, Sultanate of Oman during March 2011 and the effluent was collected from a leading vegetable oil mill in Oman.

Materials and methods

Chitosan powder of low molecular weight (20 kDa) with 80 % degree of deacetylation was purchased from sigma Aldrich, Bangalore. For pH adjustments, 1 M HCl/NaOH solutions prepared in pure distilled water of high purity were used. The amino groups in chitosan are protonated and become positively charged at low pH and its surface charge will decrease and become insoluble at high pH. The functional properties of chitosan were explained elsewhere (Anthonsen and Smidsrod 1995; Kurita 2001; Bernal et al. 1999; Domard et al. 2001; Østgaard et al. 2001; Ottoy et al. 1994). Chitosan is a linear β-1,4-linked polysaccharide, obtained by the partial deacetylation of chitin. The properties of chitosan can vary with molecular weight and degree of deacetylation. The chemical structure of chitosan has been shown in Fig. 1.

The investigations were carried out with the effluent before and after treatment. The waste water sample was collected from the outlet of an equalization tank in a vegetable oil refinery in the sultanate of Oman. The effluent samples were allowed to settle before characterization. The samples were preserved at 4 °C in order to avoid bacterial action. 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 main parameters studied are COD, electrical conductivity (EC), total suspended solids (TSS), and turbidity. COD measurements were performed by calorimetric method using spectrophotometer (AQ 400, thermo Scientific Orion and Thermo Reactor Orion COD 125). It is used to measure the oxygen demand for the oxidation of organic matters by a strong chemical oxidant which is equivalent to the amount of organic matters in sample. Dissolved oxygen was measured by DO meter, Orion 3 Star, Surface morphology by JSM-840A make scanning electron microscope (SEM), EC by electrical conductivity meter (JENWAY 4510), and turbidity by turbidity meter (WTW Turb 550). Characterization of the chitosan powder was done using SEM to visualize the quality and morphology of the adsorbent before and after treatment.

The experiments were conducted at room temperature (25 ± 2 °C) by mixing required amount of chitosan powder with 500 mL of vegetable oil mill effluent and kept under stirring. Samples were collected at definite 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 such as chitosan dosage 400 mg, pH 4, stirring speed (50 rpm) and mixing time (45 min). Subsequent experiments were conducted at optimized parameters. For COD measurement, the sample was reacted with an acidic solution of potassium dichromate in the presence of a catalyst (silver) and digested for 2 h at a temperature of 150 °C. The test results are expressed in milligrams of oxygen consumed per liter of sample (mg/l).

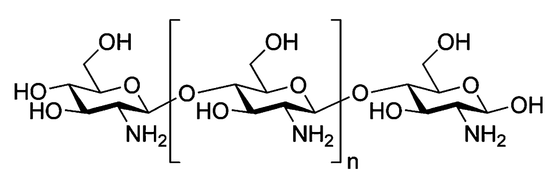

Fig. 1 Chemical structure of chitosan

The percentage removal efficiency was calculated by

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

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

The effluent concentrations of COD, TSS, EC, turbidity and DO were analyzed according to standard methods (APHA 1998).

Results and discussion

Effect of chitosan dosage

The effect of dosage of chitosan was studied by varying the amounts of adsorbent from 100 to 400 mg/l, while keeping other parameters (pH 4, agitation speed 50 rpm and mixing time 45 min) constant. The results were presented in Fig. 2, which showed the effect of dosage of chitosan on various parameter reductions. The percentage reduction in COD increased with increase in adsorbent dosage. This phenomenon could be explained based on the charge density. This is expected to be the higher dosage of adsorbent and will increase the surface area and greater will be the availability of exchangeable sites for the ions. Referring to the Fig. 2, the maximum reduction in COD was 79 % at a dosage of 400 mg, but TSS was increased due to increase in dosage of adsorbent. This may be due to the fact that over dosage of chitosan will decrease the percent reduction in TSS. Higher amount of chitosan was required to achieve the best result. This could be explained based on charge density, since chitosan has a high charge density and adsorption increased as the charge density of the polymer increased (Ariffin et al. 2005). The excess dosage will tend to destroy the polymer bridging mechanism between the particles, thereby increasing the percentage reduction in turbidity and decrease in TSS. 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. Based on the above observations, the flocs produced by chitosan appear rapidly and form a larger size, which can be easily settled, indicating that the polymer bridge is formed. This could be attributed to a large number of vacant binding sites, which are available for adsorption during the initial stages, but thereafter the occupation of the remaining vacant sites will be difficult due to the repulsive forces between the amino groups present on chitosan surface and the liquid phase. Insufficient dosage or over dosage of chitosan would result in the poor performance in parameter reduction. Therefore, it was crucial to determine the optimum dosage of chitosan to minimize the cost and increased effectiveness. For the optimum adsorbent dosage of 400 mg, chitosan recorded the highest reduction of parameters, which were 78 and 97 % in COD and turbidity reduction, respectively. The percentage reduction in TSS was in a decreasing trend whereas percentage reduction in EC followed increasing trend.

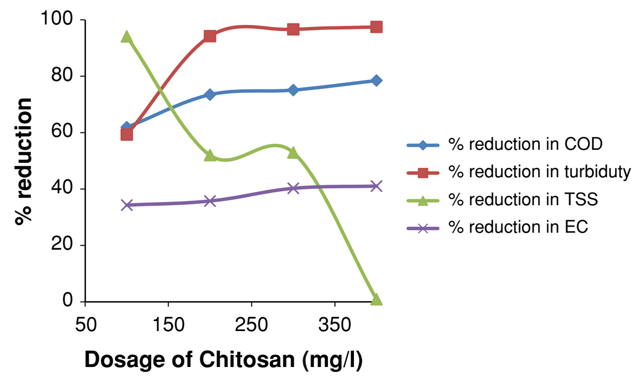

Fig. 2 Effect of dosage of chitosan (pH 4, stirring speed 50 rpm and stirring time 45 min)

The SEM micrograph of chitosan powder before and after adsorption was shown in Figs. 3 and 4. Chitosan powder before treatment has widely scattered distribution. However, this is not the case after treatment. The SEM micrograph (Fig. 4) reveals that most of the chitosan area was covered with mud-like substance and this very well shows the adsorption of particles on to the surface. These images prove that majority of the contaminants were removed and deposited on to the chitosan surface. This speaks out that crab shell chitosan is a good quality adsorbent for the treatment of vegetable oil mill effluent.

Effect of pH

Experiments were performed by varying the solution pH values from 2 to 9. The results are shown in Fig. 5. The main interaction between chitosan and oil particles is basically by electrostatic attraction. It shows that by increasing the pH while fixing the other factors changes the parameter reduction. The optimum pH for the effective removal of COD is 4 and the COD removal is not effective above pH 4. This may be due to the weak interaction between the amino groups of chitosan and oppositely charged ions present in the effluent. Furthermore, chitosan will lose its charge and become deprotonated at higher pH. In acidic conditions, chitosan would behave like a polyelectrolyte (Roberts 1992). The protonation of amino groups in chitosan makes it positively charged (act as a cationic polyelectrolyte) and since particles in the effluent are negatively charged, hence the electrostatic interaction

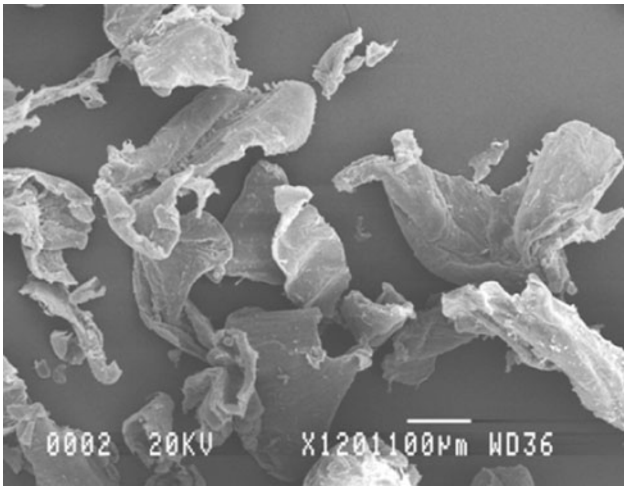

Fig. 3 SEM micrograph of chitosan powder before treatment

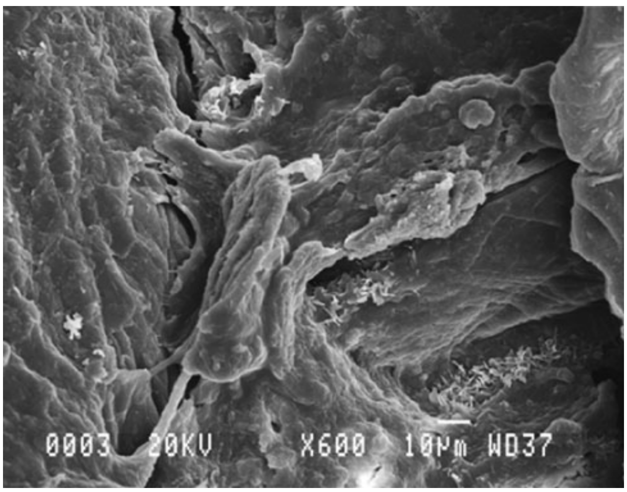

Fig. 4 SEM micrograph of chitosan powder after treatment

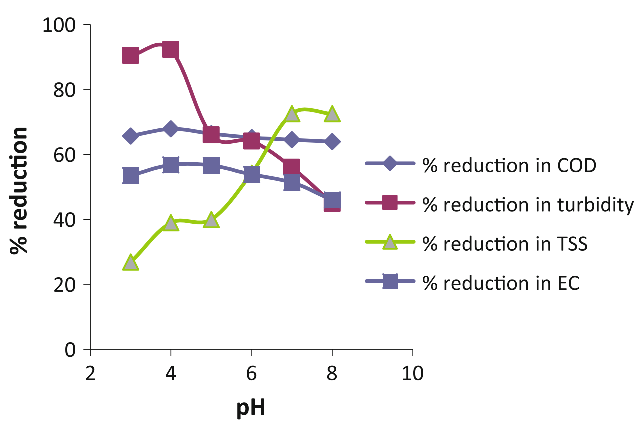

Fig. 5 Effect of pH (stirring time 45 min, speed 50 rpm and adsorbent dosage 400 mg/l)

will be strong. Chitosan is a very attractive adsorbent by allowing the molecules to bind negatively charged surface via ionic or hydrogen bonding or electrostatic interaction. This will further reduce or neutralize the particles surface charge. Therefore, pH plays an important role in parameter reductions. It is observed that the maximum percentage reduction was attained at a pH of 4. Chitosan recorded the highest COD reduction of 67 %; however, beyond pH 4, chitosan showed a slight decrease in the removal efficiencies, as illustrated in Fig. 5. This could be due to the charge reversal as well as destabilization of polymer bridging.

As demonstrated, the adsorption is highly depended on solution pH, which can be due to the surface charge of chitosan. In acidic conditions, the active site on the adsorbent is positively charged and can adsorb the negatively charged ions present in the effluent by electrostatic interaction. In basic conditions, the surface become less positively charged due to the abundance of –OH on the adsorbent which causes repulsion between the negatively charged surface and the anionic molecules, and also there are no exchangeable anions on the outer surface of the adsorbent at higher pH values, and consequently the adsorption rate decreases. By analyzing the curves, it can be stated that over 92 %, turbidity reduction was achieved at pH 4. 95 % of chitosan's amino group are protonated at pH 4 and gradually reduces as pH increased to 5 or more. Therefore, the positive charges on chitosan surface will significantly decrease as the solution pH increased; so the contribution by the charge neutralization of the chitosan to destabilize the particles becomes less important as pH increased. Percentage reduction of TSS was found maximum at pH 8, whereas the percentage reduction in EC followed a decreasing trend as pH is increased.

Effect of stirring time

Besides the effect of chitosan dosage and pH, stirring time also plays an important role in parameter reductions. An optimum contact time between chitosan and waste water to achieve effective removal of pollution load was investigated. The adsorption phenomena began immediately after the addition of chitosan. In this experiment, it was observed that the contact time of 90 min could give maximum percentage reduction in COD, EC, and turbidity. But the percentage removal in TSS shows decreasing trend. At low mixing time, the collision between the particles and chitosan surface is low, which leads to low adsorption rate.

To evaluate the effect of contact time (the stirring time) at constant rpm (50), stirring time was varied between 0 and 90 min. The results are shown in Fig. 6. As it is shown, the adsorption is very fast and the %reduction in COD was reached up to 79 %. The trend shows that maximum reduction in TSS occurred at a mixing time of 45 min. Therefore, this was selected as the optimum time for further studies. There was slight variation in EC for all mixing

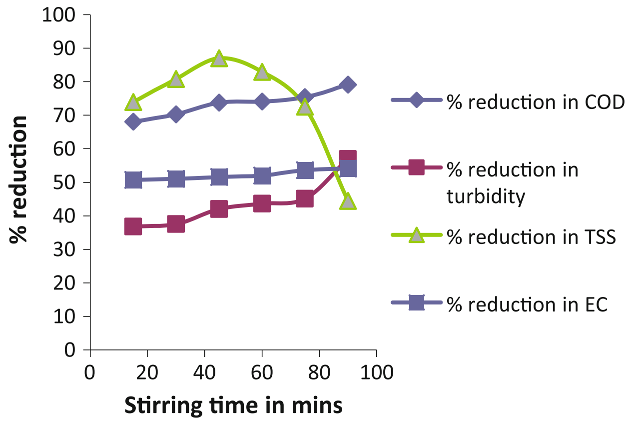

Fig. 6 Effect of stirring time (pH 4, stirring speed 50 rpm, dosage 400 mg/l)

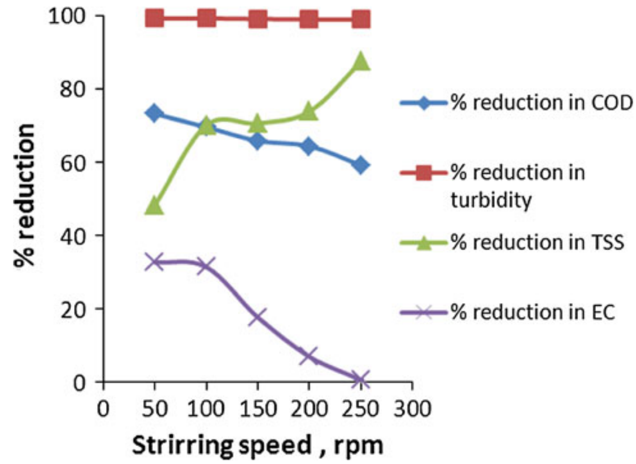

Fig. 7 Effect of stirring speed (stirring time 45 min, pH 4, dosage 400 mg/l)

times, but considerable variation in turbidity occurred throughout the experiment. The percentage reduction in TSS was lowest at 90 min. A minor variation in electrical conductivity was observed throughout the studied range of stirring time.

A significant improvement in residual water turbidity was observed with increased mixing times. The high content of amine groups in chitosan shows cationic charge at acidic pH and can destabilize colloidal suspension to promote the growth of large, rapid-settling floc that can then flocculate (Dempsey et al. 2005). As it is a long-chain polymer with positive charges at low pH, it can effectively coagulate natural particulate and colloidal materials, which are negatively charged, through adsorption, charge neutralization, inter-particle bridging as well as hydrophobic flocculation.

It was noticed that the percentage reduction in parameters increased with increase in contact time. At longer mixing time, breakage of the oil droplets is enhanced, thus reducing the particle size which results in more interfacial area for the adsorption to happen and encourages the adsorption of residue oil by chitosan. Therefore, interaction time between the oil molecule and chitosan is very important in effluent treatment.

Effect of stirring speed

The effect of stirring speed was studied by varying the speed between 50 and 250 rpm at constant concentration and stirring time of 45 min. It was observed that when the mixing speed was increased more than 50 rpm, the percentage reduction was reduced. This is due to the breakdown of oil particles and dispersed again in the sample. Mixing speed at 50–250 rpm shows a drastic reduction in suspended solids.

For an rpm of 50, the adsorption of chitosan 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 250 rpm, the percentage reductions in parameters were low. That is at higher rpm, the percentage reduction was not satisfactory due to breakdown of the expanding chain and flocs. The results indicate that there is a decrease in the extent of adsorption with increase in speed of agitation. The graphical representation of the results is shown in Fig. 7.

It has been observed that the SEM image of chitosan powder before treatment showed clear, scattered and evenly distributed morphology (Fig. 3), whereas after treatment image showed clustered and thick structure (Fig. 4), which indicates that majority of the contaminants present in the effluent are deposited on chitosan powder. This shows the effective removal of pollutants.

Conclusion

Batch adsorption study revealed that natural biodegradable chitosan of low molecular weight derived from crab shell can remove most of the colloidal and suspended organic matter and also color of the vegetable oil mill effluent. It was observed that the removal efficiency of adsorbent was optimum at a pH of 4. Also found that chitosan can be used as a very good adsorbent due to its ability in treating the effluent effectively and found minimal adsorbent dosage requirement in treatment processes. Chitosan is a natural, environmental friendly biopolymer and low cost material obtained from marine wastes, and the pollution due to fishery waste can be minimized to a great extent. 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.

Acknowledgments The authors acknowledge Mr. Salim, Sultan Qaboos University for capturing the high resolution Scanning Electron microscopy Images.

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