The Efficiency of Chitosan as a Coagulant in the Treatment of the Effluents from the Sugar Industry

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ABSTRACT

Chitosan has been used as a coagulant for industrial wastewater treatment. However, no attention has been given to the coagulation of sugar effluents using this polymer. Two effluent streams from a local sugar refinery, namely the final effluent (FE) and the resin effluent (RE) were treated using chitosan prepared by dissolution in aqueous hydrochloric acid. The optimum chitosan dosage was found to be 138 mg/l and 7.41 mg/l for RE and FE respectively, beyond which, the efficiency of the coagulant decreased. The efficiency of the chitosan was higher under acidic conditions and using sodium hydroxide to adjust the pH negatively affected the performance of the chitosan. The treatment of FE yielded better removal efficiency (97% total suspended solids, 61% colour and 35% chemical oxygen demand) than RE (68% total suspended solids, 30% colour and 15% chemical oxygen demand). This coagulant can be used to pre-treat turbid water for further treatment.

KEYWORDS: *Chitosan, Coagulation, Resin effluent, Sugar wastewater, Polymer.*

1. INTRODUCTION

Coagulation is a process used extensively in the purification of water using inorganic or organic substances known as coagulants. The performance of conventional inorganic and synthetic coagulants such as aluminium sulphate (Alum), polyaluminium chloride (PAC) and acrylamide has been established widely in literature. However, there have been health concerns about the use of these inorganic coagulants. Residues of coagulants containing aluminium and iron have been linked as a possible cause of neurological diseases such as Alzheimer disease, Parkinson disease and clinical neurotoxicity in humans.[1] This has led

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to an increasing interest in the performance of non-toxic and biodegradable coagulants. In order to remediate with the issues arising from the use of inorganic and synthetic coagulants, the performance of organic coagulant derived from naturally occurring substances is being investigated.

Chitosan is a biodegradable and non-toxic polymer, which has gained extensive attention in many fields of research and has been used as a coagulant for wastewater treatment in various industries. In recent years, it has been investigated in the wastewater treatment field as an adsorbent, a catalyst support and a coagulant among other uses. This biopolymer has been investigated as a coagulant for wastewater from various food processing industries[2-4] but very little has been published on its performance on the wastewater from the sugar industry.

The sugar refinery consumes large amounts of water daily and approximately 47% of this water is discharged as wastewater. Two streams of effluents from a local sugar refinery were considered in this study to test the efficiency of chitosan as a coagulant namely, the final effluent (FE) and the resin effluent (RE) characterized in Table 1 in terms of total suspended solids (TSS), colour, chemical oxygen demand (COD), temperature and pH.

The FE carries dissolved sugar, solids, chemicals (e.g. soda ash, sulphates, manganese etc.), ash from the boilers and other impurities from the plant general activities. The COD of this stream exceeds the limit specified by the plant's standards. It has a milky to grey colour and it is sent to the local municipality for purification. The RE is the wastewater produced from the discolouration of brown sugar syrup to yield white sugar using resin ion-exchanged. It has a high COD and a thick brown colour. Although the RE constitutes only 7% of the overall effluent from the refinery, it is more expensive to treat due to the presence of melanoidin, a natural brown polymer of high molecular mass found in sugar cane and other organic material such as molasses, coffee beans, malts, etc., which is very recalcitrant to conventional treatment methods. Thus, the RE is disposed of in authorized landfills through a waste management company. The aim of this study was to establish the feasibility of this well appraised polymer for the treatment of effluents from the sugar processing plant.

TABLE 1: Characterisation of the sugar effluents.

Parameters	FE	RE	Specified limits	DWA* guidelines
COD (mg/l)	16837	53688	<1000	75
TSS (mg/l)	309	7350	<1000	25
Colour	Milky to grey	Dark brown	Not specified	None
pH	8.5	10.02	>6.5	5.5-9.5
Temperature (°C)	25-34	34-40	25-35	25-33

Average values from January 2009 to March 2014

**DWA: Department of Water Affairs*

2. MATERIALS AND METHODS

2.1 Preparation of the coagulant

The chitosan coagulant (CCo) was prepared using a method adapted from literature.[5-7] The high molecular weight chitosan powder was purchased from Sigma Aldrich South Africa, with a degree of deacetylation greater than 75%. 100 mg of chitosan was dissolved in 20 ml of 0.1 M hydrochloric acid (HCl) in a glass beaker for 1 hour using a magnetic stirrer equipped with a hot plate at 50°C. The mixture was transferred to a one litre volumetric flask and diluted by adding distilled water to obtain a 1000 ppm bulk colourless solution with a final pH of 5 at room temperature (27°C).

2.2 Effluents collection

The effluents were collected from a local sugar refinery in Durban, South Africa for each batch of experiments. The samples were characterized (see Table 1) for chemical oxygen demand (COD), total suspended solid (TSS), pH and colour in accordance with the procedures of the refinery's quality laboratory which are in line with the South African National Standards[8] (SANS), the International Organization for Standardization[9] (ISO) and the American Public Health Association[10] (APHA).

2.3 Experimental procedure and analysis

All the experiments were performed using a non-programmable Voss flocculator (6 paddles) from the refinery's quality control laboratory (QC lab) using 300 ml glass beakers. The jar-test procedure was adapted from literature.[11,5] The chitosan coagulant (CCo) was introduced into the effluent samples using a pipette under flash mixing (100 rpm) for 3 minutes. A CCo loading of 57 mg/l CCo was used for RE and 7.41 mg/l was used for FE unless indicated otherwise. The mixing speed was then reduced to 40 rpm for 15 minutes to promote bridging and flocculation, and the solution was left to settle for 2 hours. The supernatant water was drawn out with a syringe and analysed using a Hach DR3900 UV-vis photospectrometer for COD (method 8000) and TSS (method 8006). Colour was measured using a Unicam LA 055 at a wavelength of 490 nm and a Hach pH-meter was used to measure the pH of the solutions.

The removal efficiency was calculated from the following expression:

$$\%\ \text{Removal} = \left(\frac{C_0 - C_i}{C_0}\right) \times 100 \qquad (1)$$

C_0 and C_i respectively, represent the initial values of the response variables (TSS, COD and colour) and their values after the coagulation process.

3. RESULTS AND DISCUSSION

3.1 Mechanism of coagulation using chitosan

The mechanism of coagulation of suspended particles using chitosan occurs in three steps:

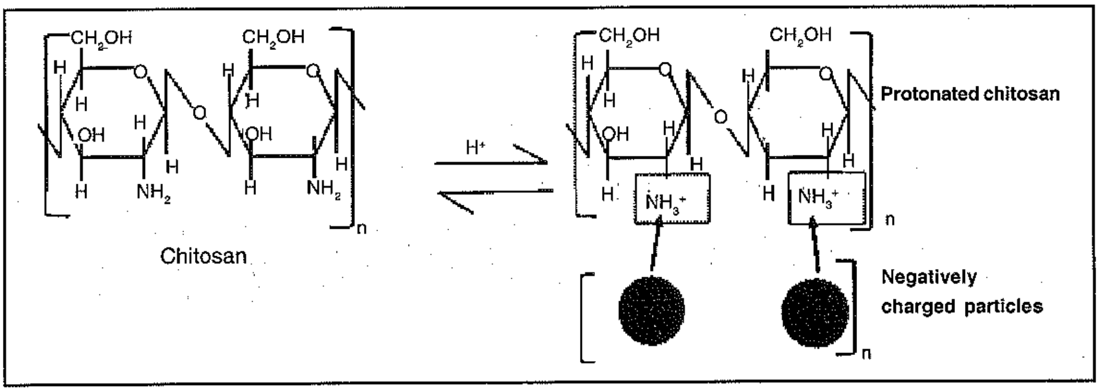

Fig. 1. Mechanism of coagulation using chitosan.

(1) the cationic charge of the protonated chitosan destabilizes and neutralizes the anionic charge of the impurities, (2) bridging of the polymer with the suspended particles leading to flocs formation, (3) electrostatic patch (EPC), which is the coagulation induced by the contact between the neutralized patches that form when an anionic particle is neutralized by a cationic material as stated in step 1.[12-14] Chitosan behaves as a coagulant and flocculant due to its long polymeric chain, the presence of NH_3^+ when dissolved in acid, the formation of bridges with the impurities, and the precipitation that occurs when the pH is above 6.5 (Fig. 1).

3.2 Effect of initial pH

The pH values of the samples were adjusted towards the acid or the basic range using HCl or NaOH. A comparative experiment was conducted between samples at natural pH (without pH adjustment) and the samples where the pH was adjusted.

From Table 2 it can be noted that when the pH of water sample was adjusted toward the acidic range using HCl a high removal of TSS, COD and colour was observed.

It was also observed (Table 2) that when experiments were conducted with samples at natural pH, the coagulant provided better results for TSS, COD and colour compared to the samples adjusted to the same pH value with sodium hydroxide (NaOH).

TABLE 2: Effect of the pH on the coagulation using chitosan

	RE						FE					
	% removal at natural pH			% removal at adjusted pH			% removal at natural pH			% removal at adjusted pH		
Sample pH	TSS	Colour	COD	TSS	Colour	COD	TSS	Colour	COD	TSS	Colour	COD
4	N/A	N/A	N/A	77	19	14	N/A	N/A	N/A	97	88	11
5	N/A	N/A	N/A	68	10	14	N/A	N/A	N/A	98	86	11
6	N/A	N/A	N/A	50	9	8	N/A	N/A	N/A	98	85	10
7	63	16	5	37	6	0	97	87	9	97	86	9
8	60	13	4	0	0	0	97	85	9	95	85	5
9	57	12	2	0	0	0	N/A	N/A	N/A	87	76	-7
10	53	11	2	0	0	0	N/A	N/A	N/A	84	74	-12

N/A: No data available from the collected sample at this pH

Samples of RE that were adjusted to basic pH using NaOH yielded poor results. Adding NaOH on the FE led to precipitation at pH above 10 without the assistance of chitosan. Although most of the solids and colour were removed by that precipitation, treatment of those samples with chitosan yielded poor results in terms of COD removal.

There are two possible explanations for the observations in Table 2:

(1) The resin effluent and the final effluent also contain lime carry-over from the carbonating station among other chemicals which may react with the NaOH or with both the NaOH and the chitosan and thus decrease the coagulation efficiency.

(2) The presence of NaOH precipitates the chitosan and impedes bridging. NaOH is used in literature to gel the chitosan in the formation of chitosan beads by solidifying the polymer as it comes into contact with the NaOH solution.[15]

It can be noted that the removal of COD for both effluents is very low. This is due to the fact that most of the COD in these effluents is caused by dissolved organics. A recent study has indicated that efficiency of the chitosan was directly affect by the initial total dissolved solids (TDS) in the water and effluents with high TDS, yielded low COD removals.[16]

3.3 Effect of coagulant loading and impurities loading

The influence of the chitosan loading in RE and FE was investigated. Figure 2 shows that the optimum chitosan concentration for RE was found to be 138 mg/l which resulted in the removal of 68% TSS, 30% colour and 15% COD. For the FE the optimum coagulant concentration was found to be 7.41 mg/l, leading to 97% TSS, 61% colour and 35% COD. Beyond these optimum values, the performance of the CCo decreased. This can be explained by the pH-dependent behaviour of chitosan. Under acidic conditions the chitosan is completely protonated from NH_2 to NH_3^+. The NH_3^+ neutralizes the negative charges of the impurities, entrapping them into the long polymeric chain (bridging) and form flocs. As the flocs increases in size under slow mixing (40 rpm) they settle out.

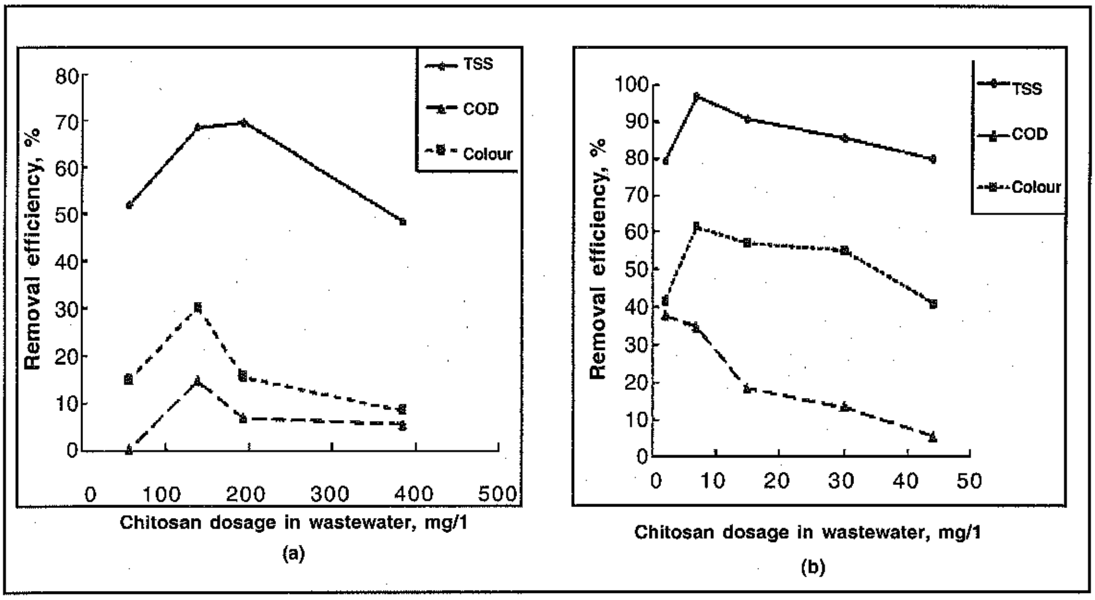

Fig. 2. Effect of coagulant loading on TSS, COD and colour removal for (a) RE and (b) FE.

Overdosing the coagulant destabilizes the neutralized flocs and impedes their settling. Excessive amount of chitosan increases the amount of NH_3^+ present in the effluent and the neutralized flocs begin to repel each other and the protonated chitosan. The excess chitosan in this case forms gel-like film on the surface of the sample.

Chi and Cheng[4] studied the effect of chitosan as a coagulant for wastewater from the milk processing industry. They reported that the impurity removal efficiency increased with an increase in chitosan dosage. They also stated that as the dosage increased continuously, the reversal of chitosan surface charge occurred, leading to a decrease of the removal of turbidity and COD.

Divakaran and Sivasankara Pillai[6] reported that after the optimum dosage was reached, no advantage was obtained by increasing the dosage of chitosan for their treatment of kaolinite in suspension in water. A similar observation was made by Bina et al.[5]

It can be noted from Figure 2 that the optimum chitosan loading for RE was approximately 20 times higher than the amount needed for the FE. This can be explained by the difference in impurities content between the two effluents (See Table 1). The RE carries a higher pollution load than the FE, and therefore requires more chitosan to neutralize the impurities in order for coagulation to occur. At lower impurity concentrations, there are few solids in the water and a larger amount of the coagulant remains suspended and/or dissolved in the water thus increasing the COD values due to the organic nature of chitosan.

4. CONCLUSION

The treatment of sugar industry resin effluent (RE) and final effluent (FE) using chitosan was investigated under various conditions. It was found that increasing the chitosan dosage increased the impurities removal efficiency for the response variables investigated. However, beyond the optimum coagulant concentration no further improvement was observed. The optimum chitosan loading was found to be 138 mg/l for the RE and 7.41 mg/l for the FE. The impurity content in the effluent was found to influence the amount of chitosan loading required.

The performance of the chitosan was found to be pH-dependent and high removal efficiencies were achieved under acidic conditions. The addition of NaOH considerably reduced the coagulation efficiency, possibly gelling the polymer.

Chitosan was able to remove most of the suspended solids and decrease the cloudiness of the FE. Although the CCo failed to remove the COD which is the major concern of the refinery, its efficiency for TSS removal and potentiality for high colour removal makes it a good pre-treatment method for this effluent. Using effluents at natural pH saves costs on chemicals for pH adjustment and protects equipment from damages caused by acidic conditions.

The health benefits of chitosan in the water treatment field and the fact that the production of chitosan from crustaceans shells is good methods of reducing pollution from the fishery industry, makes chitosan a good product to use for wastewater treatment as well as a good alternative to the inorganic coagulants.

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