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Influence of Effluent Type on the Performance of Chitosan as a Coagulant

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Abstract: The use of chitosan as a bio-polymeric coagulant has continued to attract interest in water treatment due to its biodegradability and non-toxicity. Its ability to treat effluents of high organic content has been investigated in some food processing industries. The focus of the present study is to compare results of the use of chitosan in the treatment of effluent from a Sugar Processing Plant (SPP), with those obtained from the treatment of wastewater from a Milk Processing Plant (MPP) and from a Brewery Processing Plant (BPP), in order to determine the influence of effluent type on the impurities removal efficiency.

The treatment of the MPP provided the best removal efficiency (99% suspended solids removal and 70% COD removal) in comparison to the SPP (98% suspended solids removal and 11% COD removal) and BPP (95% suspended solids removal and 50% COD removal). The optimum pH value varied as a function of the type of effluent with BPP= 4.5, SPP = 4.5 and MPP =7. The results indicate that chitosan is not very efficient for the removal of dissolved matter. A relationship between total suspended solids (TSS) and total dissolved solids (TDS) has been developed.

Keywords: Chitosan, coagulation, wastewater, model.

I. INTRODUCTION

There are various methods for the treatment of polluted water, these include among others; evaporation, membrane technology, activated carbon adsorption, biological treatment, chemical and electrochemical treatments (precipitation and coagulation).

Evaporation is an effective and non-toxic way of treating polluted wastewater since there is no need to add chemicals to the process and the condensate is relatively clean water. However, it is inefficient for large scale operations due to the high energy consumption and it poses a problem of solid disposal. Biological treatment involves the action of living microorganisms that utilize the waste material as food and convert it into simpler substances by natural metabolic processes. This process is eco-friendly, but slow. Membrane technology and filtration is also effective but can be costly especially for highly polluted water. Adsorption using activated carbon has been proven efficient for the removal of dissolved particles. However, the cost requirement of the carbon regeneration is a major disadvantage. Electrochemical treatment method is attractive due to its low toxicity, and its efficiency in removing the impurities in the water. But this method is not sustainable for large scale applications [1].

Chemical treatment such as coagulation using inorganic salt and synthetic polymers has been widely used in the treatment of wastewater to remove solids and other impurities. The use of inorganic salts such as alum has become a health concern with reports of illnesses such as Alzheimer disease among others associated with prolonged consumptions of the traces of these chemicals in the water [2]. To remediate with the hazardous effect thereof, inorganic salts are combined with organic or synthetic polymers. Although this combination provides many advantages such as good coagulation efficiency, lower quantity of sludge, ease of dewatering and filtration, their prolonged health impact has not yet been established [3, 4].

There is a growing interest in the use of natural coagulant in wastewater treatment, most of them aiming to plant or animal waste and process them into bioplolymers. Wastes such as crustacean shells from the seafood industry pose a problem due to the fact that they degrade at very slow rates, and in some countries these waste are disposed of on landfills posing a problem of land space [5-7]. Seafood shells however, contain a non-toxic, biodegradable polymer know as chitin. The chitin extracted from the shellfish and crabs is often converted into chitosan by chemical treatment which has more economical value than chitin due to its wider range of application. Chitosan is capturing the attention of scholars mostly as an adsorbent in water treatment for the removal of impurities such as heavy metals and colour among many others [5, 8, 9].

Chitosan is a polymer of β-(1–4) linked 2-acetamido-2-deoxy-β-D-glucopyranose and 2-amino-2-deoxy-β-D-glycopyranose prepared by deacetylation of chitin. Chitosan is protonated by weak acid in aqueous solution under the pH of 6.5. The protonated chitosan forms bonds with the negatively charged impurities in three steps: (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 and flocs formation, (3) electrostatic patch [10, 11]. The protonation of chitosan occurs as follow:

$$Chit\text{-}NH_2 + H^+ \longrightarrow Chit\text{-}NH_3^+ \quad (1)$$

Although the use of chitosan as a coagulant has been widely documented, the behaviour of this polymer appears to be affected by the type of impurities contained in the wastewater being treated. This work reviews the results from two published articles treating different kinds of effluents from different food and beverage industries namely, the wastewater from milk processing plant (MPP) and the wastewater from brewery processing plant (BPP) with chitosan and compares it with experimental works conducted at a sugar refinery in Durban, South Africa.

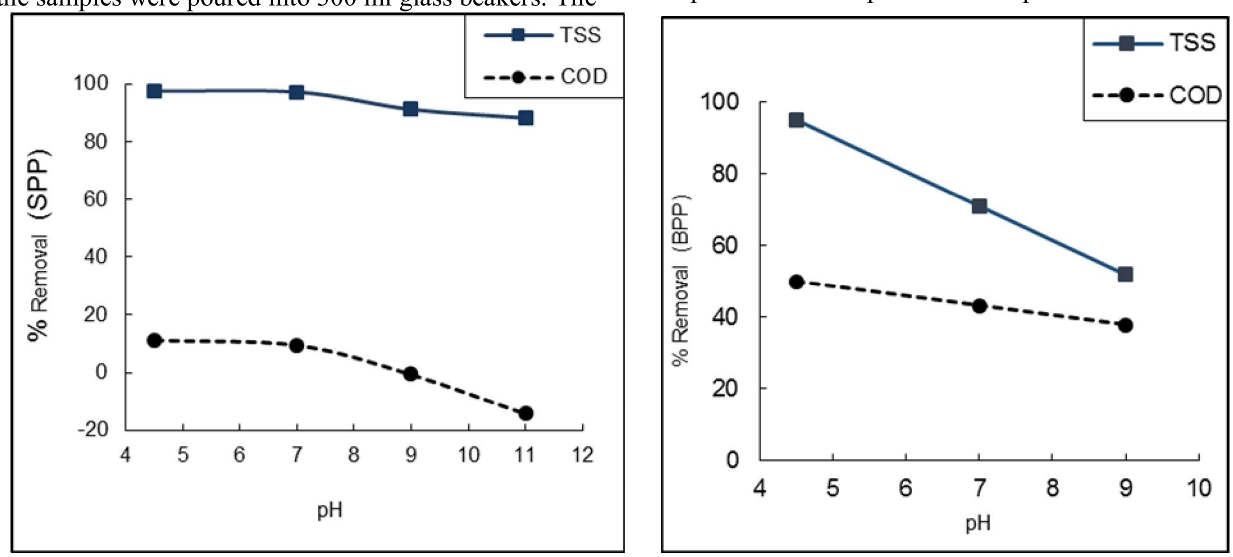
II. Materials and Methods

Chitosan was purchased from Sigma Aldrich with a 75% degree of deacetylation was used as coagulant for the final effluent from a Sugar Processing Plant (SPP). The coagulant was prepared by dissolving 100 mg of chitosan in 20 ml of 0.1 M hydrochloric acid (HCl). The mixture was stirred for one hour using a magnetic stirrer with stove at 50°C. The effluent was collected on site from the refinery's dam and used without further dilution. It was then diluted to make 1000 ppm of colourless bulk solution (pH $\leq$ 5). Portion of this bulk solution was further diluted to 100 ppm for the purpose of the experiments. Fresh coagulant was prepared for each batch of experiments.

All the experiments were performed using a non-programmable Voss flocculator (6 paddles) jar-test apparatus where the samples were poured into 300 ml glass beakers. The coagulant was added to the samples under rapid mixing (100 rpm) for 3 minutes. The mixing speed was then reduced by 60 % for 15 minutes and the solution was left to settle for a maximum of 2 hours. The supernatant water was drawn out using a syringe and analysed using a photospectrometer (Hatch DR 3800) using method 8000 for chemical oxygen demand (COD) and method 8006 for total suspended solids (TSS). The methodology for the MPP and the BPP are similar to the one stated above and can be found in the published articles by Ref. [12] and Ref. [13] respectively. The effluent were collected and analysed in accordance with the South African National Standards (SANS), the American Public Health Association (APHA) and the International Organisation for standardisation (ISO). The SPP is made of all the effluents generated in the refinery to the exception of the resin ion-exchange effluent, which is disposed of under different conditions. The SPP is sent off the refinery's dam where a portion of it is recycled back as cooling water for various equipment and the other part is sent to the municipality for purification. Samples were collected daily at the dam for the experiments which took place at the refinery's quality control laboratory.

III. Results and Discussion

The efficiency of chitosan in the removal of TSS and COD for the three industrial wastewaters is shown in figure 1. It can be observed that the performance of the chitosan is influenced by the pH of the effluent. The optimum pH value of the BPP was found to be in the acidic region, whereas the MPP provided acceptable result for pH values of up to 9.



(a) (b)

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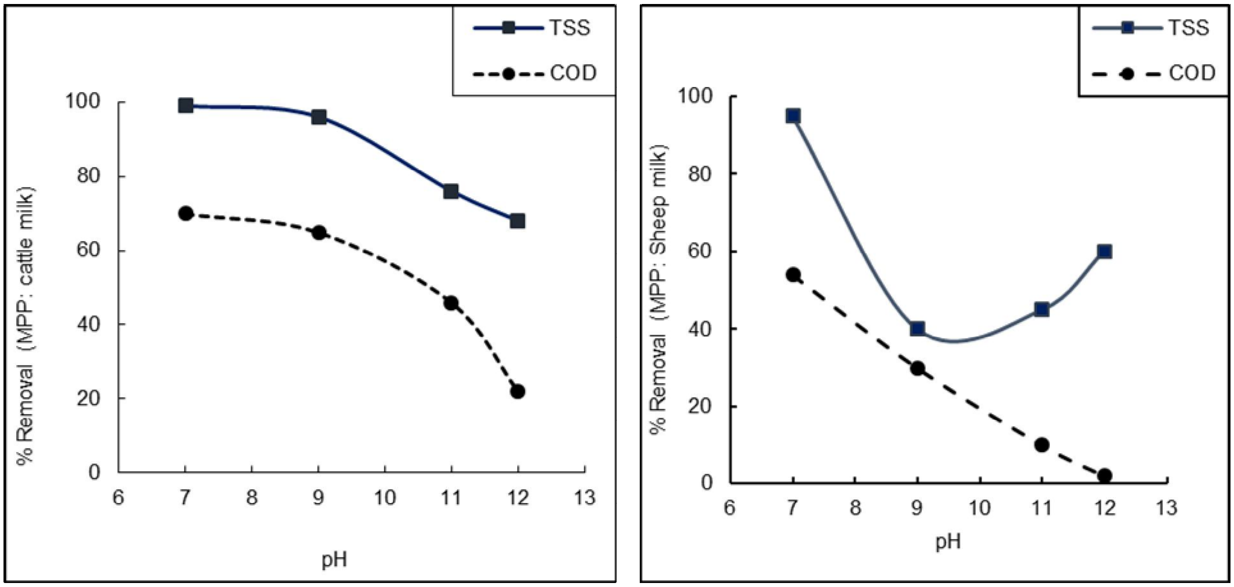


(c) (d)

Fig. 1. The influence of pH on the COD and TSS removal for (a) SPP (b) BPP adapted from Ref. [12] (c) MPP from cattle milk adapted from Ref. [13] and (d) MPP from sheep milk [13]

In the case of SPP, the performance of chitosan was higher at acidic pH (4.5) and good results were obtain up to pH 7 (97%) above which the efficiency of the coagulant decreased. However the performance of the chitosan for COD removal in the SPP was less than 11%.

This can be explained by the nature of the impurities in each of the effluents. Milk is composed of colloids in suspension water-based liquid, only 30% of the COD in the MPP from cattle milk is due to dissolved solids (TDS). In the case of MPP from sheep milk it can be seen the COD removal is lower compared to the MPP from cattle milk due to the fact that 96% of its COD is caused by dissolved particles. The use of the coagulant neutralizes the charge of the suspended particles in the MPP causing it to agglomerate into flocs and settle. Therefore, since the most impurities in this effluent is caused by organic matters in suspension (such as lipids, proteins, etc.), the use of the chitosan was able provide a high percentage removal for both TSS and COD compared to the SPP and the BPP.

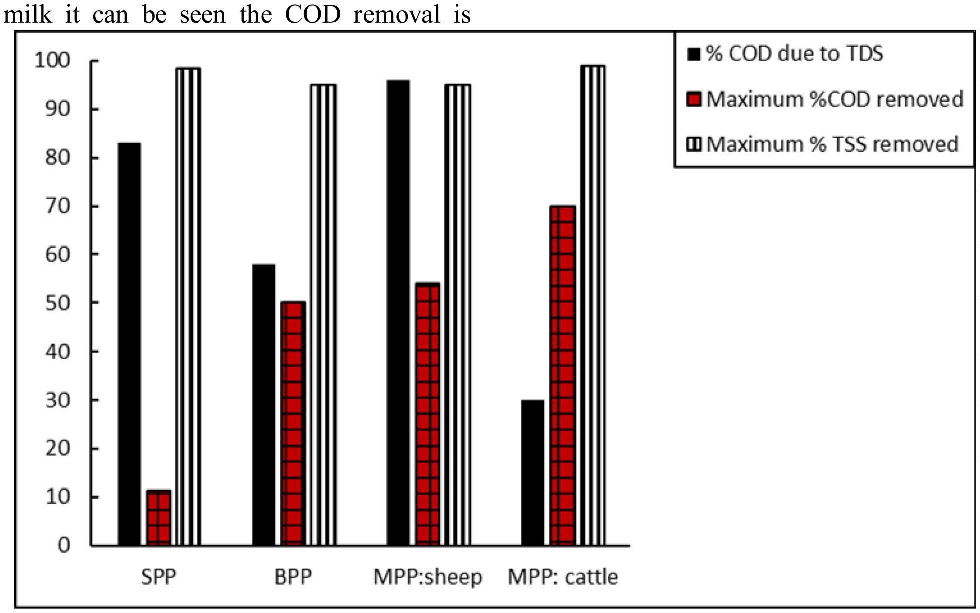


Fig. 2. Relationship between COD due to TDS, and impurities removal

It can also be seen from figure 2 that chitosan is not very efficient to remove dissolved organics from the wastewater. Ref. [14] reported that the coagulation process is generally less efficient for the removal of TDS than TSS. In the case of the SPP where approximately 80% of COD is caused by dissolved sugar and other organic matters, the maximum COD removed was only 11% which is insignificant compared to 50% for the BPP, 54% and 70% for MPP for sheep milk and cattle milk respectively.

The impurities in the wastewater also has an effect on the amount of coagulant required. In general, only the TSS (or turbidity) of a sample is taken into account when selecting the coagulant dosage range. However, the coagulant dosage is affected by a combination of factors such as the initial TSS of the effluent, the TDS, the chemical components in the effluent and the pH of the water [15] [16]. The coagulation process depends on the amount of particles in the wastewater. If the amount of colloids in the water is high, the coagulant forms larger flocs which settles readily, whereas at low turbidity there is insufficient amount of particles attaching themselves to the polymer, therefore the formation of smaller and lighter flocs [17]. A higher dosage of coagulant is required for high turbidity water to ensure that all the particles are neutralized. This explains the low dosage obtained for the SPP (7.41mg/l). Although the MPP carries more suspended solids than the BPP, it requires a lower dosage (15 mg/l for sheep milk and 25 mg/l for cattle milk) than the latter (120 mg/l for BPP) due to its low TDS and the nature of the impurities it carries. The removal of TSS to be more affected by the amount of suspended solid present in the effluent and the chitosan dosage used. This can be seen in figure 2. For all these effluent under optimum conditions, the removal of TSS was above 90%.

A model was developed, taking into account the ratio of initial TSS to the initial COD (α), the COD due to TDS (β) and the initial TSS value (δ) for all four effluents.

Table. 1. Relationship between TSS, TDS, COD and coagulant efficiency

	α (COD/TSS)	β ($\frac{COD_f}{COD_t}$ x100)	δ (TSS)	Chitosan dosage, mg/l (Y_1)	% COD removed (Y_2)	% TSS removed (Y_3)
SPP	0.09	83	385	7.41	11	98
MPP: Sheep	8.29	96	7410	15	54	95
BPP	0.28	58	2100	120	50	95
MPP: Cattle	3.6	30	19485	25	70	99

α = Total COD (mg/l) divided by the TSS (mg/l); β represents the percentage COD due to TDS as a fraction of the COD after filtration (mg/l) to the total COD (mg/l) times 100; δ is the TSS in mg/l.

The relationship between α, β and δ was deduced as follows:

$$Y_1 = 481.50371 + 26.73309\alpha - 5.64972\beta - 0.019669\delta \quad (2)$$

$$Y_2 = 155.41543 + 11.24058\alpha - 1.73455\beta - 3.78983\text{E-}003\delta \quad (3)$$

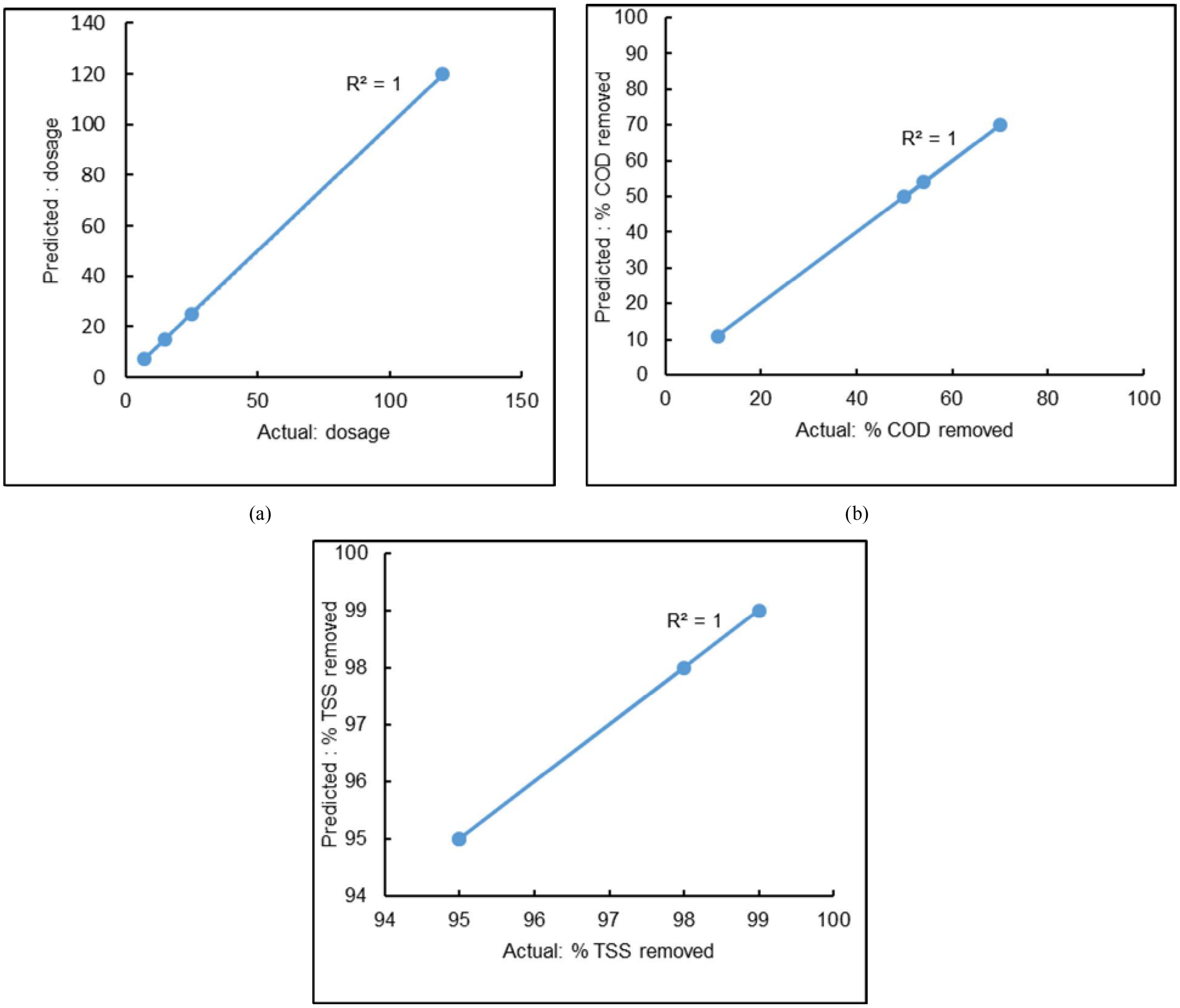
$$Y_3 = 84.52538 - 1.24147\alpha + 0.16033\beta + 7.25385\text{E-}004\delta \quad (4)$$

The constraints for the model equations above can be expressed by considering the interaction between the values of α and β.

If $\alpha < 0.1$ and $\beta > 50$, the removal of COD will be lower than 50%, increase the value of β above 80 reduces the COD removal efficiency below 15%. This constraints however, does not affect the TSS removal considerably.

If $\alpha > 1$ and $\beta < 55$, the removal of COD and TSS increase, while the dosage required decreases as well.

The dosage required decrease for value of α below 0.1 and increases as this value augments (for $\beta > 50$).



(a) (b)

(c)

Fig. 3. Comparison between the actual responses and the predicted responses for the models (a) dosage, (b) % COD removed and (c) % %TSS removed.

The model was tested against the findings from Ref.[18] for wastewater from olive oil mills (OMW) and the wastewater from the winery (WW) and the results are presented in table 2. The article did not present the values of the COD after filtration, so in this case an arbitrary value of β was used.

Table. 2. Model validation

	OMW			WW		
	α	β*	δ	α	β*	δ
	7.93	50	6700	2.07	50	750
	Actual	Predicted		Actual	Predicted	
Y_1 (Dosage, mg/l)	400	279		20	240	
Y_2 (COD removed, %)	32	132		72	89	
Y_3 (TSS removed, %)	81	88		92	91	

* The value for β was assumed to be 50% for both wastewater

From table 2, it can be seen that Y_3 (Eq.4) is the only regression that provided a good fit for both OMW and WW. Y_2 predicted a value close to the actual response for the removal of COD for WW but failed to predict the response for OMW. The regression model Y_1 failed to fit for both effluents.

IV. Conclusion

The efficiency of the chitosan is directly related to the type of effluent being treated. Factors such as TDS content, initial TSS, was found to influence the coagulation process. Although chitosan is generally reported to perform better under acidic conditions, it was found that, depending on the nature of the impurities in the wastewater, the efficiency can be stretched up to a pH value of 9.

It was found that chitosan was not very efficient for the removal of dissolved matters (TDS). In the case SPP and sheep milk effluent where most of the COD is caused by the presence of dissolved particles and other substances, the amount overall COD removal was lower compared to BPP (58% of COD is caused by TDS) and cattle milk effluent (30% of the COD is due to TDS). It was also found that the optimum pH value differed with the type of effluent (BPP: 4.5; SPP: 7; MPP: 7).

However, the influence of the type of effluent is not very considerable in terms of suspended solid removal, which was found to be more affected by the amount of suspended solid and the chitosan dosage used. The difference in COD removal for the various effluent is very noticeable (MPP: 99% and 95% suspended solid removal, 70% and 54%COD removal for cattle and sheep milk effluents respectively. SPP: 98% suspended solid removal and 11% COD removal. BPP: 95% suspended solid removal and 50% COD removal). The nature of the impurities in the effluents was also found to affect the cost of the purification process, the quality and the volumes of the sludge produced for each of the effluents investigated.

Modelling the responses for this treatment method (dosage, COD and TSS removal efficiency) reflected an effluent-dependent behaviour on the efficiency of the chitosan as a coagulant. The regression for TSS removal provided a good fit for two other effluents.

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