



Efficacy of Chitosan as a Coagulant Aid to Alum Precipitation of Congo Red In Wastewater

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Abstract

The use of chitosan prepared from prawn shells as coagulant aid for congo red (CR) dye removal from wastewater was investigated in this study. Characterisation of the prepared chitosan samples showed characteristics similar to commercially available ones. The coagulation – flocculation experiment was carried out using the jar test procedure. Both chitosan and alum were used separately for the dye precipitation and then combined together. The usage of alum alone showed no precipitating effect on the CR dye molecule, while chitosan was able to considerably reduce the concentration of the dye in solution. When chitosan was used as a coagulant aid in the alum precipitation, the amount (%) of dye removed increased greatly. Optimization of the process via study of effect of pH and flocculation time at optimum alum – chitosan combination indicated that pH 4-5 and settling time of 40 min were suitable conditions for maximum decolourisation of CR dye wastewater with about 98% efficiency. Moreover, study of settling characteristics of the sludge produced from the alum-chitosan synergy was better than that produced from either of them alone. Also, occurrence of redispersion and restabilization of the precipitate was not encountered.

Keywords: Alum; Chitosan; Coagulation; Dye; Flocculation; Sludge.

1. Introduction

Numerous technological processes are assessed to remove colour and colour-impacting substances from wastewater. Colour in water (true or apparent) is the first contaminants to be recognized in any wastewater and gives an indication that such water has been polluted. The direct discharge of coloured wastewater into water bodies induces aesthetic problem that could decrease the amount of sunlight penetrating into the waterbody thus disturbing photosynthetic activity and biological processes of the aquatic bodies and reduction of the dissolved oxygen [1]. Wastewater generated from many industrial processes contains huge residues of inorganic/organic compounds with complex structures (e.g dyes and pigments) recalcitrant to degradation and often rich in colour [2]. Heightened interest in the treatment of dye (coloured) effluent is prompted due to their possible direct toxicity. Many dyes are made from aromatic compounds, some of which are carcinogenic, such as benzidine and susceptible to biotransformation. For example, reduction of azo- and nitro- compounds in sediments and intestinal environments, resulting in the regeneration of the parent toxic amines have being reported [3, 4]. Over 100,000 commercial dyes are available and classified either as, anionic (direct/ reactive) dyes, cationic dyes or nonionic (disperse dyes). Industries are recently charged with stringent effluent treatment regulations to reduce the colour content in their wastewater before discharge into the surface water. Decolourization of industrial effluent is assessable via the following methods: Adsorption, Filtration, Precipitation, Chemical degradation, Photo degradation and biodegradation [1, 5]. The mechanism of colour removal is achievable either by concentrating the colour into sludge, partial breakdown or complete breakdown of the colour molecule. Adsorptive treatment is the most frequently employed for the treatment of coloured effluents because of the availability of numerous materials (adsorbents) such as activated carbon, resins, agricultural wastes, microorganisms and biopolymers [1, 6]. Adsorptive treatment is however limited in use due to high cost incurred in the purchase of sorbents and regeneration and safe disposal of sorbate-laden materials. Biological processes such as aerated lagoons, activated sludge and white rot fungi are commonly cited for the treatment of coloured effluents [7]. However, colour is not readily removed from biological-based treatment processes due to the high stability of the colour imparting species [8]. Physical treatments such as membrane process using nanofiltration and rapid sand filtration have also been reported [9], but are besieged with the production of huge voluminous sludge that requires disposal. Photochemical, catalytic and electrochemical degradation processes are also used for the removal of colour from industrial wastewater [10]. These methods though efficient, their effectiveness are hampered with high energy costs and formation of hazardous by-products.

Physico-chemical treatment involving coagulation and flocculation processes have shown to be simple to operate, efficient and cost-effective [11, 12]. Coagulation and flocculation processes are used to separate the suspended solids portion from the water to overcome the forces destabilizing the suspended particles, allowing particle collision and growth of floc. Coagulation and flocculation occur in successive steps: charge neutralization, self-association to form large size aggregates (coagulation), separation of the aggregates from solution by filtration/floatation (flocculation) and separation of flocs by sedimentation. The floc is separable and their removal is facilitated by sedimentation. The use of conventional coagulants (alum, ferric chloride, lime, polymers) in wastewater treatment has attracted less attention due to the problems associated with their use [13]. Focus is now on the use of coagulants-flocculants of natural origins. Natural coagulants referred to as biocoagulant are categorised as plant-, animal- or microorganism- based, and are characterised with non-toxic, biodegradable, cheap, ready availability and abundant, environmentally friendly, etc [6]. The use of natural polymers as biocoagulants presents the following advantages over the conventional synthetic ones: completely biodegradation of sludge generated and no toxicity to the environment, [14]. Examples of biocoagulants that have been used include, *moreiga oleifera*, chitosan, *nimral* seed, *jatropha curcas*, tannis, extract of alginate etc [15-21].

Chitosan has received a great deal of attention for the past 20 years for many applications in wastewater treatment as adsorbent and coagulant [5, 22]. Chitosan is a biopolymer constituted of glucosamine and acetylglucosamine units with high molecular weight obtained from polysaccharides. It has drawn particular attention as an effective biosorbent / biocoagulant due to its low cost compared to activated carbon and its high contents of amino and hydroxyl functional groups showing high reactivity potential for various organic pollutants (Fig. 1). It is seen as an attractive alternative to other biomaterials because of its physico-chemical characteristics, chemical stability, high reactivity and selectivity towards varied pollutants. The presence of the amine groups confers interesting cationic properties in acidic solutions.

Fig-1. Schematic Representation of Chitosan Preparation from Chitin

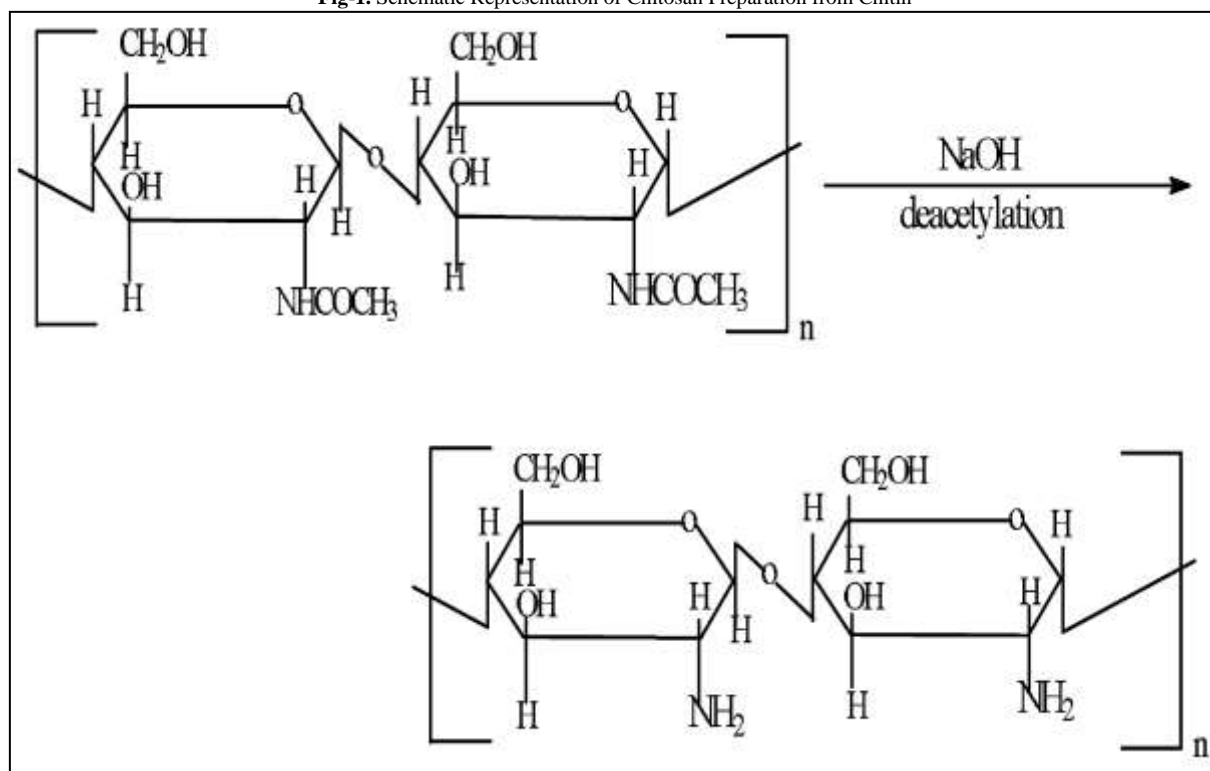
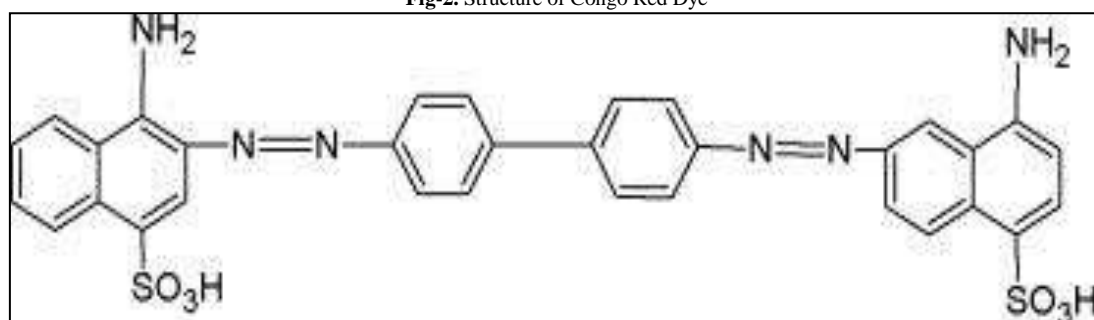


Fig-2. Structure of Congo Red Dye



The present study investigated the use of chitosan as a coagulant aid to alum for the coagulation and flocculation of industrial wastewater prepared from synthetic feed solution of CR as an economical method towards appropriate technology. Nigeria is a third world country with many small and medium scale industries incapacitated for huge

extensive capital investments and operational costs needed to set up a treatment plant to clean up their industrial effluent generated before discharge to surface bodies. Thus, environmental and economic future of developing nations necessitated this study.

2. Materials and Methods

2.1. Materials

All the chemicals used were of analytical grade (Merck, Germany). Shells of prawns purchased from Malaysia were used to prepare chitosan samples. The deacetylation (Fig. 1) of the prawn shells was achieved by heating it with 80% NaOH solution of ratio 1:14 (w/v) for 6 h with intermittent stirring for homogenous reaction. The resulting chitosan was washed to neutrality using distilled water, filtered and air-dried. The chitosan sample prepared was tested by dissolving it in 1% acetic acid and characterised. The functional groups present on the surface of the chitosan samples were determined using Fourier Transform infrared spectrophotometer (FTIR, Thermo Scientific, USA). The degree of deacetylation of the chitosan samples was calculated by:

$$DD = 100 - \frac{A_{1600}^{-1} / 1.33}{A_{3450}^{-1}} \times 100 \quad (1)$$

Where, DD is deacetylation degree, $A_{1660\text{cm}^{-1}}$ and $A_{3450\text{cm}^{-1}}$ are absolute heights of absorption band of amide and hydroxyl groups. The weight of the wet sample was determined after 24 h and then dried to constant weight to determine the dried weight. Moisture content of the chitosan sample was determined using gravimetric method, by drying the sample to constant weight and measuring the weight of sample before and after drying. The difference in the weights gives the moisture content by:

$$\% \text{ moisture content} = \frac{\text{Wet weight (g)} - \text{Dry Weight (g)}}{\text{Wet Weight (g)}} \times 100 \quad (2)$$

Ash content of chitosan samples was determined thus: 2 g of sample was placed into a previously heated and cooled crucible and heated in a muffle furnace preheated to 650°C for 4 h. The crucible was allowed to cool in the furnace to less than 200°C and then placed in a desiccator. Ash content in the sample was determined by:

$$\% \text{ Ash Content} = \frac{\text{Weight of residue (g)}}{\text{Sample weight (g)}} \times 100 \quad (3)$$

2.2. Methods

2.2.1. Coagulation-Flocculation Experiment

The coagulation and flocculation studies of the synthetic coloured water were conducted using the jar test method. The conventional jar test procedure with a six-unit multiple stirrer system (75 x 25 mm) was used in a batch. Each batch consists of rapid mixing, slow mixing and sedimentation process. The coagulant was added to samples of the dye solution and rapid mixing was performed at 200 rpm for 3 min to allow flocs to formed, followed by a slow agitation (flocculation process) at 40 rpm for 20 min for settling. The sedimentation process allows the precipitate to settle at the bottom of the jar. Samples were collected after 30 min of settling in the upper part of the beaker for filtration using 0.22 μm glass fiber filters. Filtered samples were analysed using a UV-Vis Spectrophotometer (UV-1601, Shimadzu) at the λ_{max} of the dye. The ability of alum as a primary coagulant for the decolourisation of dye solution of initial concentrations (10 - 100 mg/L) was assessed at varying alum dosages (0.1 - 1.0 mg/L). The ability of chitosan as primary coagulant was carried out at dosages of 1 g/L – 8 g/L. Optimum alum / chitosan dosage combinations was determined at optimum (fixed) alum dosage and varying chitosan concentrations and vice versa. Studies of effects of flocculation time (10 - 120 min) and pH (3-6) on the coagulation process were carried out at optimum chitosan/alum combinations.

2.2.2. Preparation of Synthetic Dye Wastewater and Calibration Curve

The dye used in the present studies is Congo red; a typical benzidine-based azo dye, widely found in the effluent of industries. Congo Red (CR) is an azo dye and sodium salt of benzidinediazo-bis-1-naphthylamine-4-sulfonic acid. The characteristics and molecular structures of the dye are shown in Fig. 2 and Table 1. The stock CR dye solution (500 mg/L) was prepared by dissolving an appropriate amount of the dye into double - distilled water. Working solutions of varied concentrations (10-100 mg/L) were prepared from the stock by serial dilution with the double - distilled water. The residual dye solution concentrations (mg/L) were determined by finding out the characteristic absorbance wavelength obtained at the λ_{max} via a UV/visible spectrophotometer. Calibration curve was plotted using the absorbance and concentration of standard dye solution. The curve obtained from the plot was used to determine the concentration of the residual dye solutions. The percentage (%) colour removed was calculated using the formular:

$$\% \text{ Dye Removal} = \frac{c_o - c_e}{c_o} \times 100 \quad (4)$$

Where c_o (mg/L) is the initial dye concentration and c_e is the final dye concentration after the treatment process (mg/L).

Table-1. Physicochemical Properties of Congo Red dye

Parameter	Properties
Molecular weight	696.66 g/mol
Molecular formula	C ₃₂ H ₂₂ N ₆ Na ₂ O ₆ S ₂
Absorption maxima	490 nm
Dye class	Azo
Odour	Odourless
Solubility	Soluble in ethanol and acetone, Insoluble in ether
pKa	4.1; 3.0
Solution pH	8-9.5

3. Results and Discussion

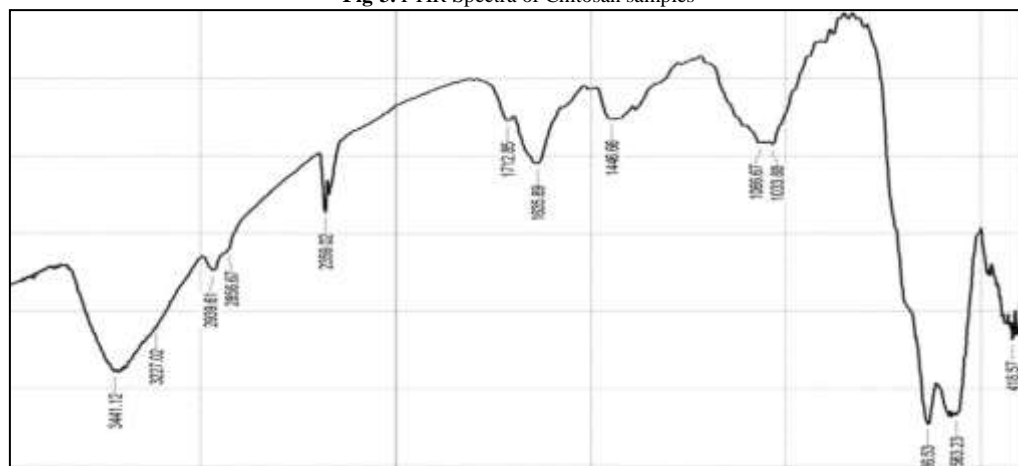
3.1. Characterisation of Biocoagulant

The physicochemical properties of the prepared chitosan samples conform (Table 2) to that reported in literatures [23, 24]. Commercial chitosan has been reported to have ash content of 1.18% [25]. According to Hossein, *et al.* [23], the moisture content of chitosan from prawn is in the range of 1.0 - 1.30 %, what was obtained from this study was 1.26. The degree of deacetylation (DD) calculated by using Eqn. 1 and FTIR analysis, (Figure 3) was 80%. The value of DD is usually affected by the source and preparation procedure and usually ranges between 30 – 95 % [26]. The low ash content of the sample (1.19 %), was an indication of effectiveness of the demineralization step for removal of mineral materials.

Table-2. Physicochemical Properties of Chitosan Samples

Moisture (%)	Ash (%)	DD (%)	M.Wt (g/mol)	Solubility
1.26	1.19	80	105	1% Acetic acid

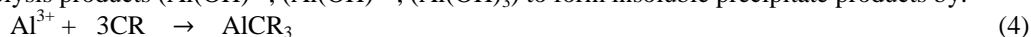
The FTIR spectra depicting the functional groups present on the surface of the chitosan samples from FTIR analysis is given in Fig. 3. FTIR spectra of the chitosan sample gave characteristics bands at 3404.37cm⁻¹ attributed to -NH₂ and -OH groups stretching vibration while the band at 1656.91cm⁻¹ was attributed to the stretching vibrations of amide group carbonyl bonds in the infrared spectrum of chitosan [27]. The characteristic carbonyl stretching of chitosan was observed at 1755.28 cm⁻¹. Chitosan absorption peak corresponding to the amine groups were observed at 1558.54 cm⁻¹ [28]. Other notable peaks characteristics of chitosan were observed at 2922 cm⁻¹, 2877 cm⁻¹ [29]. According to Awang and Aziz [30]; Aziz, *et al.* [31], coagulation-flocculation effective groups are carboxyl, hydroxyl and amino (amine and amide) groups which were all detected in the chitosan sample. These groups (hydroxyl (O-H) and carboxyl (C=O)) help in promote flocculating efficiency through bridging.

Fig-3. FTIR Spectra of Chitosan samples

3.2. Coagulation experiment

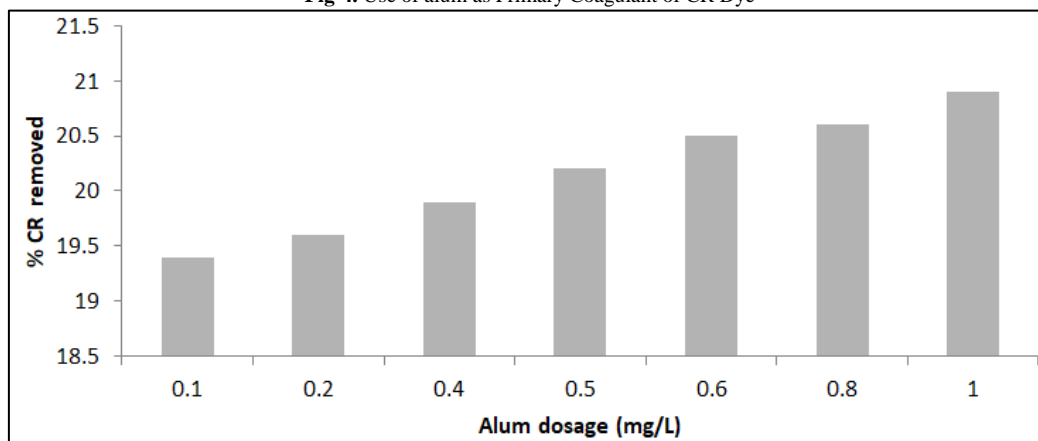
3.2.1. The use of Alum as Primary Coagulant for Dye Removal

Alum precipitation of CR dye molecules was conducted at different concentrations of the dye (10-100 mg/L) and varying dosages of the alum (0.1 – 1.0 mg/L). The results obtained (Fig. 4) indicated that negligible reduction in the amount of dye was achieved with the addition of alum solution. Moreover, at constant CR concentration, increase in alum dosage had no appreciable precipitating effect as a coagulant on the coloured effluent. Colour (Natural Organic Matter) removal from solution is achieved via charge neutralization or adsorption [32, 33]. In the present study, CR removal by alum was expected to occur based on electrostatic interaction. This is because the products of the ionization of both the CR dye molecules and alum in aqueous medium are oppositely charged. Normally, electrostatic attraction is expected between the acid dye and aluminium ion (Al³⁺) or alum cationic hydrolysis products (Al(OH)²⁺, (Al(OH)²⁺, (Al(OH)₃) to form insoluble precipitate products by:



According to [Jessey and Sydney \[34\]](#), the insoluble basic salt formed from the electrostatic interaction causes precipitation leading to the decolourisation of the solution and removal of coagulant compounds ($\text{Al}_3(\text{SO}_4)$ from solution. What was obtained was however, contrary as depicted in Fig. 4. Several reasons are given for this occurrence: (i) unfavorable operating pH. (ii) Low concentration of coagulant and (iii) Low molecular weight. It could be assumed based on the results obtained that these three factors influenced the reaction greatly. For example, it is probably that the experiment was carried out at a pH that was not favourable for complete ionization of the functional group on the dye molecule that prevented the formation of the insoluble basic salt. Also, considering the molecular weight of alum (252.192 g/mol) the formation of the insoluble basic salt may not be possible due to its relatively low weight. If at all, the loose flocs formed are not dense enough for easy macroflocs formation and subsequent sedimentation [\[35\]](#).

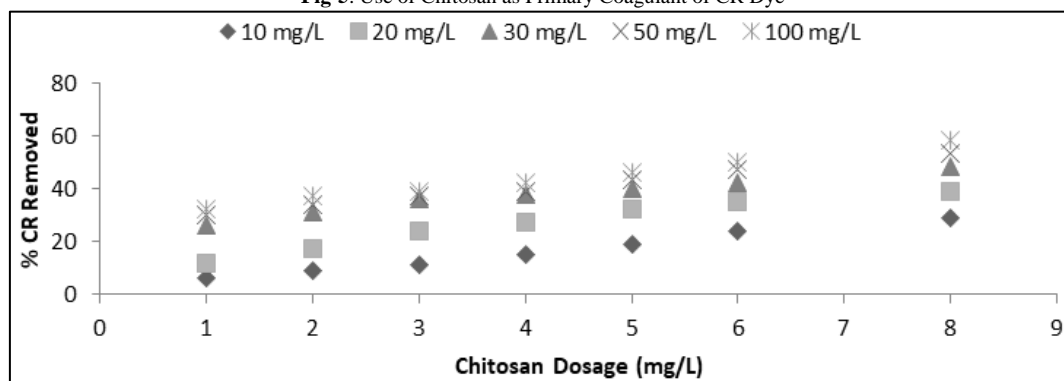
Fig-4. Use of alum as Primary Coagulant of CR Dye



3.2.2. The use of Chitosan as a Primary Coagulant

The ability of chitosan as a primary coagulant was tested at different dosages of chitosan solution (1-8 g/L) and different concentration of dye (CR) solution (10-100 mg/l). Results obtained presented in Fig. 5 are expressed as percentage of dye removed. It was observed that dye removal from the solution increased with increase in the chitosan dosage for each dye concentration. Moreover, the percentage of dye removed increased with increase in the initial dye concentration. In this study, the addition of chitosan solution to the dye solution produced water with low residual dye concentration. According to the classical theory of coagulation-flocculation, colloidal particles removal from aqueous system could occur through different mechanisms; compression of double electric layers, neutralization, adsorption, bridging and/or sweep flocculation [\[36\]](#). Possible mechanism of interaction between chitosan and the dye is proposed thus: CR as an anionic dye produces a highly negative charge surface in solution, while chitosan the biocoagulant gives a cationic hydrolysis product as a result of the protonation of the amine group. Charge neutralization between the anionic CR and the cationic chitosan biocoagulant is therefore expected. This suggests the possibility of columbic interaction between the anionic CR dye and chitosan molecules to form insoluble neutral products [\[8\]](#). The probably interactions between the biocoagulant chitosan and dye CR could be either precipitation or adsorption of the dye on the surface of the chitosan via chemical or physical interactions. It is also possible that the removal of the colour particles was also through bridging flocculation mechanism because of the high molecular weight of the biocoagulant (Table 2). Coagulants with high molecular weights are more effective in improving the bridge – formation of suspended particles thereby causing rapid size development of flocs. The weight of the dye-loaded chitosan will cause its sedimentation readily in the solution.

Fig-5. Use of Chitosan as Primary Coagulant of CR Dye



3.2.3. Effect of Alum-Chitosan Synergy

This experiment was conducted at fixed alum concentration (500 mg/L) and varying chitosan dosages (g/L). The results obtained presented in Fig. 6 indicated an increase in the amount (%) dye removed compared to when alum and chitosan were used separately as the primary coagulant. As the initial dye concentration was increased from 10

mg/L to 100 mg/L, the amount of dye removed (%) also increased from 43.5% to 89.3%. The probable mechanism of removal could be sweep coagulation brought about by the increase in the colloidal load of the aqueous system as a result large surface area of the chitosan promoting its sedimentation. Further study on the alum-chitosan combination synergy was assessed by optimizing alum dosage on chitosan application as a biocoagulant aid in the decolourisation of the CR dye contaminated wastewater. This study was carried out using the different optimum chitosan dosages in combination with alum dosages (0.1-1.0 mg/L). Results obtained indicated an improvement in the decolourisation of the dye contaminated wastewater (Fig. 7). Optimal dosages for alum- chitosan combination synergy was found to be at 0.8 mg/L for alum while chitosan was 5 g/L for effective CR wastewater decolourisation at the initial dye concentrations studied.

Fig-6. Determination of Optimum Chitosan Dosage in Alum- Chitosan combination

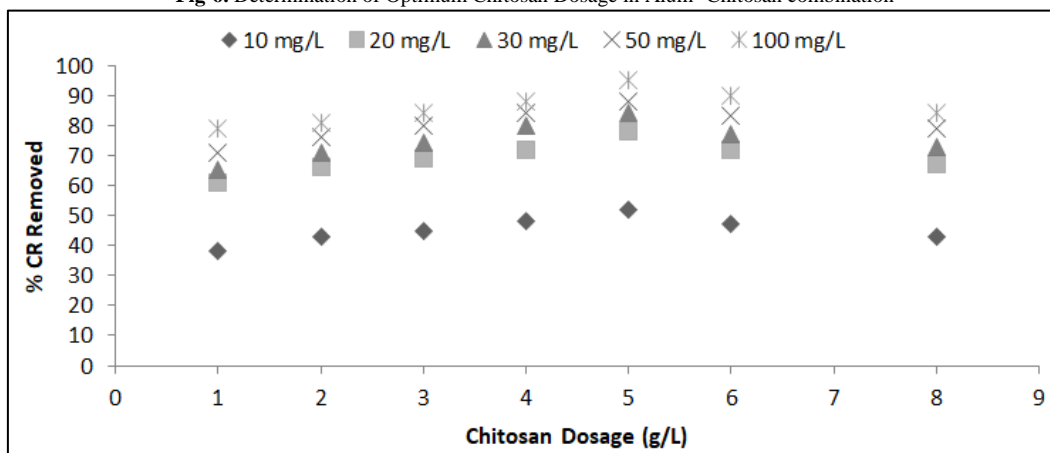
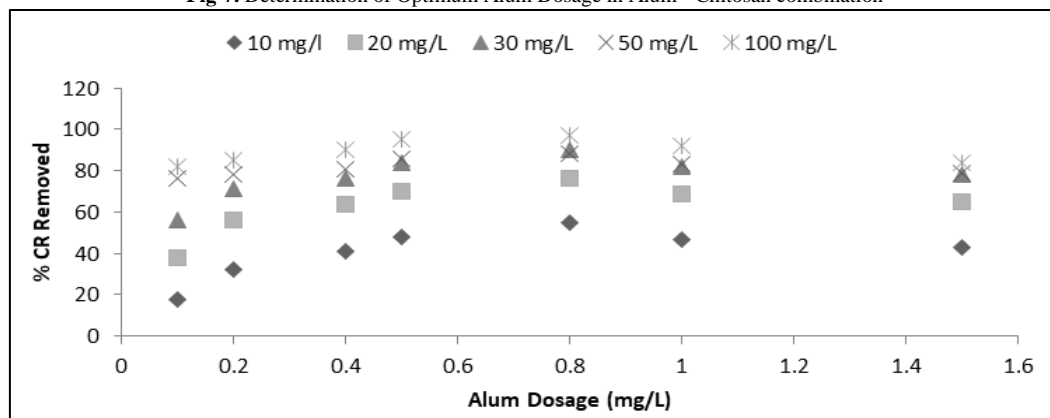
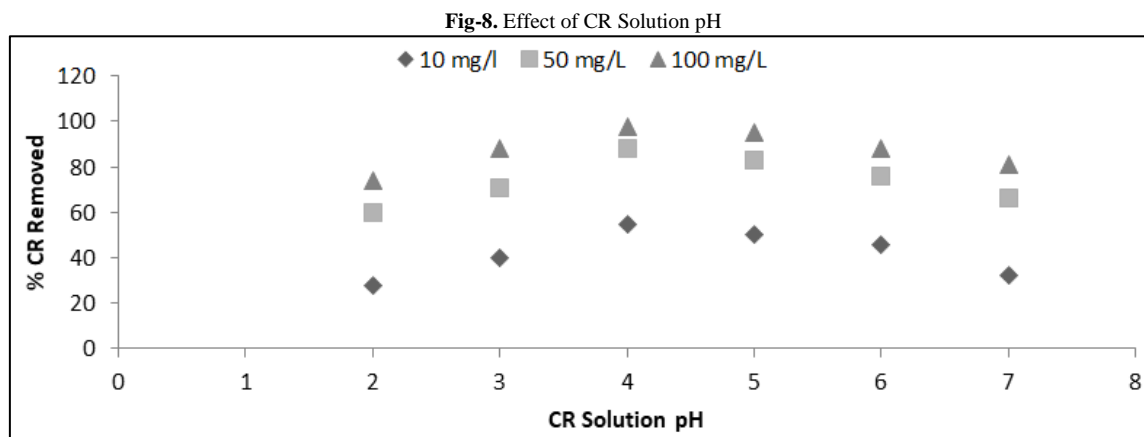


Fig-7. Determination of Optimum Alum Dosage in Alum - Chitosan combination



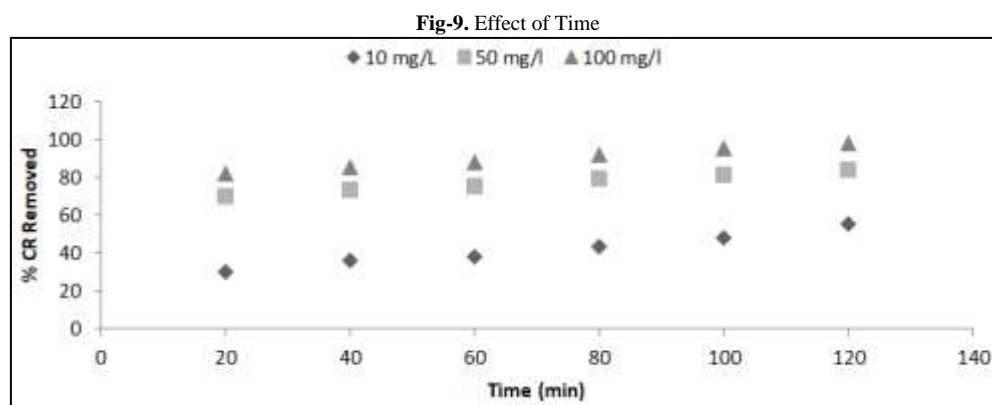
3.2.4. Effect of CR Solution pH

Coagulation- flocculation processes are highly pH dependent. At acidic pHs, metal hydrolytic products of the metal coagulant are outplayed by H^+ ions for organic ligand and poor removal occurs with precipitation of some of the organic acids. At alkaline pHs, OH^- ion competes with the organic compounds for metal adsorption sites and the precipitation of metal hydroxide occurs by co- precipitation. To optimize the effect of pH for CR removal from aqueous solution, a pH range of 2-7 was selected. This range was chosen because alum coagulation is generally effective at pH limits of 5.5 to 8.0 [8, 37]. The experiment was conducted at optimum alum/chitosan dosages and the initial dye concentrations of 10, 50, and 100 mg/L were used. From the results obtained presented in Fig. 8, it was observed that CR dye removal (%) was appreciable at all the pH ranges used but the highest removal (%) of the dye occurred at pHs 4 and 5. The reason ascribed for this observed trend is, the hydrolysis products of the metal coagulant (alum) at pHs slightly below its minimum solubility (6.3) are medium polymers/ monomers very effective in removing dissolved particles (organics/metals) [35].



3.2.5. Effect of Time

The flocculation time which is the time given to macrofloc formation is a very key important factor in coagulation- flocculation process in a water treatment plant industry. The experiment on effect of flocculation time on CR removal from aqueous system was conducted at the optimum alum/chitosan dosages, pHs and flocculation time range between 10-120 min. Results obtained presented in Fig. 9 showed that optimum time for dye removal was at 40 min after which, no significant removal was achieved. Notably, redispersion and restabilisation of flocs at higher flocculation time did not occur with the use of chitosan as a coagulant aid to alum in CR removal from aqueous system over the entire 120 min of study.



4. Conclusion

Alum decolourisation of CR dye wastewater was not effective but greatly enhanced with the use of chitosan as a coagulant aid. The decolourisation process was more efficient at pH 4-5 and flocculation time of 40 mins. Chitosan is therefore proposed as an effective coagulant aid to alum in decolourisation of anionic dye wastewaters.

References

- [1] Ho Nicholas, Jian, H., and Nurhazwani, I., 2018. "Removal of Dye in Wastewater by Adsorption-Coagulation Combined System with Hibiscus sabdariffa as the Coagulant MATEC " In *Web of Conferences*. p. 01008.
- [2] Roussy, Chastellan, M., Vooren, E., and Guibal, 2005. "Treatment of ink-containing wastewater by coagulation/flocculation using biopolymers." *Water SA*, vol. 31, pp. 369-376.
- [3] Jiang, C., Fu., Cai, H., and Cai, T., 2016. "Efficient adsorptive removal of Congo red from aqueous solution by synthesized zeolitic imidazolate framework-8, Chem. Speciat." *Bioavailab*, vol. 28, pp. 199-208.
- [4] Verma, A. K., Dash, R. R., and Bhunia, P. A., 2012. "A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters." *J. Environ. Manage.*, vol. 93, pp. 154-168.
- [5] Roussy, VanVoopren, M., and Guibal, E., 2004. "Chitosan for the coagulation and flocculation of mineral colloids." *J. Disper. Sci. Technol.*, vol. 25, pp. 663-677.
- [6] Vijayaraghavan, G. and Shanthakumar, S., 2015. "Removal of sulphur black dye from its aqueous solution using alginate from Sargassumsp. (brown algae) as a coagulant, Environ." *Prog. Sustainable Energy*, vol. 34, pp. 1427-1434.
- [7] Bell, J. and Buckley, C. A., 2003. "Treatment of textile dye in the anaerobic baffled reactor." *Water SA*, vol. 29, pp. 129-134.
- [8] Oladoja, N. A., Aliu, Y. D., and Ofomaja, A. E., 2011. "Evaluation of snail shell as a coagulant aid in the alum precipitation of aniline blue from aqueous solution." *Environmental Technology*, vol. 32, pp. 639-652.
- [9] Springer, A., 1985. *Industrial environment control: Pulp and paper industry*. John Wiley.

- [10] Oladoja, N. A. and Aliu, Y. D. Y. D., 2009. "Snail shell as coagulant aid in the alum precipitation of malachite green from aqua system " *Journal of Hazardous Materials*, vol. 164, pp. 1494-1502.
- [11] Kim, T.-H., Park, C., Shin, E.-B., and Kim, S., 2004. "Decolorisation of disperse and reactive dye solutions using ferric chloride." *Desalination*, vol. 161, pp. 49-58.
- [12] Zaino, N. A., Aziz, H. A., Yusoff, M. S., and Umar, M., 2011. "The use of polyaluminium chloride for the leachate treatment of landfill leachate via coagulation and flocculation process." *Res. J. Chem. Sci.*, vol. 1, pp. 34-39.
- [13] Adelagun, R. O. A., Ngana, O. C., and Ezekiel, E., 2016. "Evaluation of egg shell as a coagulant aid in dye removal from aqueous system." *J. of Fuw Trends in Sci. and Tech.*, vol. 1, pp. 591-594.
- [14] Vijayaraghavan, G., Sivakumar, T., and Kumar, A. V., 2011. "Application of plant based coagulants for waste water treatment." *International Journal of Advanced Engineering Research and Studies*, vol. 1, pp. 88-92.
- [15] AWWA, 2005. *Water treatment plant design*. Mc Graw Hill, pp. 1-15.
- [16] Malakootian, M. and Fatehizadeh, 2010. "A. Color removal from water by coagulation/caustic soda and lime Iran." *J. Environ. Health. Sci. Eng.*, vol. 7, pp. 267-272.
- [17] Naimabadi, A., Movahedian Attar, H., and Shahsavani, A., 2009. "Decolonization and biological degradation of azo dye reactive red2 by anaerobic/aerobic sequential process." *Iran. J. Environ. Health. Sci. Eng.*, vol. 6, pp. 67-72.
- [18] Ndabingsere, A. and Narasiah, K. S., 1998. "Quality of water treated by coagulation using Moringa oleiferera seeds." *Water Res.*, vol. 32, pp. 81-791.
- [19] Ozacar, M. and Sengil, I. A., 2000. "Effectiveness of tannins obtained from valonia as a coagulant aid for dewatering of sludge." *Water Res.*, vol. 34, pp. 1407-1412.
- [20] Ozacar, M. and Sengil, I. A., 2003. "Effect of tannin on phosphate removal using alum." *Turk. J. Eng. Environ. Sci.*, vol. 27, pp. 227-236.
- [21] Beltran-Heredia, J. and Sanchez-Martin, J., 2009. "Improvement of water treatment pilot plant with Moringa oleiferaextract as flocculant agent. " *Environmental Technology*, vol. 30, pp. 525-534.
- [22] Strand, S. P., Varum, K. M., and Ostgaard, K., 2003. "Interactions between chitosan and bacterial suspension-adsorption and flocculation." *Colloids Surface B.*, vol. 27, pp. 71-81.
- [23] Hossein, T., Mehran, M., Seyed, M. R. R., Amir, M. E., and Farnood, S. S. J., 2008. "Preparation of chitosan from brine shrimp (*Artemiaurmiana*) cyst shells and effects of different chemical processing sequences on the physicochemical and functional properties of the product." *Molecules*, vol. 13, pp. 1263-1274.
- [24] Terbojevudith, M. and Cosani, A., 1997. *Molecular weight determination of chitin and chitosan. In chitin handbook*. European Chitin Society: Muzzarelli, R.A.A and Peter M.G. eds. . pp. 87-101.
- [25] Wang and Kinsella, J. E., 1976. "Functional properties of novel proteins: alfalfa leaf protein." *J. Food Sci.*, vol. 41, pp. 286-292.
- [26] Martino, A., Turner, A., and Millward, G. E., 2003. "Influence of organic complexation on the adsorption kinetics of nickel in river waters." *Environmental Science and Technology*, vol. 37, pp. 2383-2388.
- [27] Chatterjee, S., Lee, M. W., Lee, D. S. W., and Woo, S. H., 2009. "Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate." *J. Hazardous Mater*, vol. 166, pp. 508-513.
- [28] Marchessault, R. H., Ravenelle, F., and Zhu, X. X., 2006. "Polysaccharides for drug delivery and pharmaceutical applications." *American Chemical Society*, p. 368.
- [29] Wang, Turhan, M., and Gunasekaran, S., 2004. "Selected properties of a pH- sensitive biodegradable chitosan- poly(vinyl alcohol) hydrogel." *Polym. Int.*, vol. 53, pp. 911-918.
- [30] Awang, N. A. and Aziz, H. A., 2012. "Hibiscus rosa-sinensis leaf extract as coagulant aid in leachate treatment." *Appl. Water Sci.*, vol. 2, pp. 293-298.
- [31] Aziz, H. A., Alias, S., Adlan, M. N., Faridah, A. H., and Zahari, M. S., 2007. "Colour removal from landfill leachate by coagulation and flocculation processes." *Bioresour Technol*, vol. 98, pp. 218-220.
- [32] Gregor, J. E., Nokes, C. K., and Fentin, E., 1987. "Optimizing natural organic matter removal from low turbidity water by controlled pH adjustment of alum coagulation." *Water Res.*, vol. 31, pp. 2949-2958.
- [33] Randtke, S. J., 1988. "Organic contaminant removal by coagulation and related process combinations." *J. Am Water Works Assoc.*, vol. 80, pp. 40-56.
- [34] Jessey, M. C. and Sydney, A. H., 1971. *Coagulation and flocculation, in Water quality and treatment: A Handbook of Public Water Supply, Prepared by American Water Works Association Inc.* 3rd ed. McGraw Hill Books, pp. 66-111.
- [35] Yan, M., Wang, D., Ni, D., Qu, J., Chow, C. W. K., and Liu, H., 2008. "Mechanism of natural organic matter removal by polyaluminium chloride: effect of coagulate particle size and hydrolysis kinetics." *Water Res.*, vol. 42, pp. 3361-3370.
- [36] Stephenson, R. J. and Duff, S. J. B., 1996. "Coagulation and precipitation of a mechanical pulping effluent removal of carbon, colour and turbidity." *Water Res.*, vol. 30, pp. 781-792.
- [37] Mall, I. D., Srivastava, V. C., Agarwal, N. K., and Mishra, I. M., 2005. "Adsorptive removal of malachite green dye from aqueous solution by bagasse fly ash and activated carbon—kinetic study and equilibrium isotherm analyses, Colloids Surface A: Physicochem." *Eng. Aspects*, vol. 264, pp. 17-28.