TREATMENT OF WASTEWATER PRINTING INK BY PROCESS COAGULATION USING CHITOSAN NANOPARTICLES

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ABSTRACT

In the present study, chitosan nanoparticles were used for the treatment of colored solutions by coagulation–flocculation (as an alternative to more conventional processes such as sorption). Effluent discharge of printing ink waste water contains high colour, suspended solid and dissolved organic pollutants was selected as a model waste water treatment for verifying chitosan nano particles. Study on the wastewater characteristics, effluent flow measurement, wastewater treatments to determine the process system of wastewater treatment has been carried out. Batch coagulation experiments were conducted to evaluate the influence of initial pH (4.0-7.0) and coagulant dosage 10-50 mg on colour removal from solution. Residual colour, total suspended solid(TSS), COD and system pH were observed as function of time. Optimum pH was found to be 5.0 for the coagulants. Optimum dosage chitosan nanoparticles was found to be 28 mg respectively, giving 99.8 % colour removal efficiency in 25 min. Reduction efficiency of Total Suspended Solid (TSS) of 95% with the TSS concentration of 106 mg/L, COD of 94% with the COD concentration of 500 mg/L. The flocs were recovered and the dye was efficiently removed using alkaline solutions (0.001–1 M NaOH solutions) and the biopolymer, re-dissolved in acetic acid solution, was reused in a further treatment cycle.

KEYWORDS: Coagulation, Dissolved Organic, Suspended Solid, Colour, Chitosan Nanoparticles

INTRODUCTION

To ensure the preservation of water resources from the disposal of wastewater of printing ink industry, the government of Indonesia has set effluent quality standards for industrial effluent. In order to fulfill effluent quality standards, the wastewater of printing industry must be treated by physic-chemical or biological processing or a combination of physic-chemical-biological wastewater which is dependent their characteristics. When wastewater contains high suspended solids and low dissolved organic concentration, this wastewater is enough treated by physic-chemical process with the treated wastewater fulfilling the effluent quality standard. But, when the wastewater contains high dissolved organic and low suspended solid content, this waste water needs biological treatment process in order fulfill the effluent quality standard [1]

Coagulation/flocculation processes have been widely used as pre-treatments to remove suspended particles and colouring materials in primary treatment which compounds such as $Al_2(SO_4)_3.18H_2O$ and/or polymer are added to wastewater in order to destabilize the colloidal materials and cause the small particles to agglomerate into larger settle able flocks. Colloidal particles having this very small size can not settle itself and difficult to be handled by physical treatment and can only be settled after inter neighbor coagulated beforehand with the help of the addition of chemical coagulants and coagulant aid or flocculants. Through the process of coagulation, the robustness of colloidal particles dispensed to form a small flock which can then be put together through a flocculation process. The efficiency of the coagulation-flocculation method depends on the raw wastewater characteristics, pH and temperature of the solution, the type and dosage of coagulants, and the intensity and duration of mixing [2]

Recently, chitosan nanoparticles, a biopolymer of glucosamine, showed a higher capacity for adsorption of colorant than activated carbon No and Meyers [3] demonstrated that swollen beads of chitosan exhibit superior sorption capacity compared with flakes. Guibal's group [4] published a series of papers on the ability of chitosan to act as an effective coagulant to treat not only particulate suspensions but also dissolved substances. In particular, they showed that colour can be removed either by adsorption onto solid-state chitosan or by coagulation/flocculation using dissolved-state chitosan nanoparticles. The reactivity of amine groups was significantly increased when dissolved biopolymer was used [5]. The authors explained their results by the fact that using chitosan nano particles in the dissolved state improves the accessibility and availability of reactive sites compared to the solid state [6].

Bough and coworkers [7] demonstrated the effectiveness of chitosan for coagulation and recovery of suspension solid (SS) in processing wastes from a variety of food processing industries including poultry, eggs, cheese, meat, fruit cakes, seafood and vegetables. These studies indicated that chitosan can reduce the SS of such processing waste by as much as 65% to 99% and good results were also obtained for the reduction of turbidity (TB) and chemical oxygen demand (COD).

The effectiveness of chitosan as coagulant has also been reported by Johnson and Gallanger [8], These authors clearly demonstrated that chitosan has an intrinsic capacity to be used as a coagulant to reduce SS, TB and COD. These works also reported that positively charged cationic macromolecules can destabilize the negative colloidal suspension by charge neutralization as well as by bridge formati. Sanghi and Bhattacharya [9] showed that chitosan, as coagulant aid, is very effective for decolouring acidic and direct dyes. They also reported that reactive dyes with anthraquinone groups were the most difficult to decolour.

Gandjidoust et al. [10] reported that the natural coagulant chitosan resulted in the highest removal in both colour and TOC as compared to synthetic polymers (poly(acrylmide) or PAM, poly(ethyleneimine) or PEI and a chemical coagulant (alum). Similar conclusions were reported by Rodrigues et al. [11] for the treatment of paper pulp and paper mill wastewater. Renault, et al [12] has also proposed modified chitosan based biopolymers as adsorbents and/or coagulants for the removal of SS; COD and colour from pulp and paper mill effluent.

In this work we attempt to utilize chitosan nanoparticles to study examines the coagulation–flocculation of a model dye (reacrive Red 120) using as a coagulant–flocculant. To optimize the conditions for chemical pretreatment of acid orange 10, studies were undertaken to evaluate the effects of dosages of coagulants, pH

MATERIALS AND METHODS
Material

Sodium hydroxide (Merck), glacial acetic acid (Merck), sodium tri polyphosphat (merck), Chitosan of low molecular weight with a deacetylation degree (DD) of ca. 86,7% was supplied by Laboratory Analytical Chemistry, Dept of Chemistry, State University of Jakarta,

Wastewater from Printing offset PT Kalam Mulia was used. This wastewater contains Total Suspended Solid (TSS) of 85-106 mg/l, Chemical Oxygen Demand (COD) of 310 - 550 mg/l, pH of 10.4 – 11 and colour 100=250 mg/L. Influent and effluent samples of WWTP were taken and collected in plastic bottles for analysis of TSS and COD. pH of the wastewater samples was measured in situ, whereas the samples for analysis of TSS and COD were preserved according to the Standard Methods for Examination of Water and Wastewater, AWWA 2005 (Standard Methods, 2005).

Preparation of Chitosan Nano Particles Nanoparticles

Chitosan 500 mg was dissolved in 100 ml acetic acid 1% (v/v) to obtain chitosan solution, and raised to pH 4.6-4.8 with 10 N NaOH. STPP(1%) with pH 6.0 was slowly dropped into a chitosan solution. Under magnetic stirring at room temperature, 1 ml STPP 1% solution was added dropwise to 25 ml of chitosan solution. The mixture was stirred for a further 20 min followed by sonification. The resulting suspension was subsequently centrifuged at 12.000 rpm for 10 min. We added additional STPP into supernatant after centrifugation, and observed a milky emulsion, which implied that not at all the chitosan had been converted to nanoparticles. The mixture was stirred again for a further 20 min followed by sonification. The resulting suspension was subsequently centrifuged at 12.000 rpm for 10 min. The chitosan nanoparticles were obtained by freezing the emulsion at -4^0C. The frozen emulsion was then thawed in the atmosphere and the nanoparticles were precipitated and then dried at 100 °C for 96 h.The Chitosan nanoparticles was characterized by X-Ray Diffractometry, Fourier Transform Infrared spectrometry and TEM.

Coagulation–Flocculation Experiments

Experiments on dye coagulation and flocculation were performed using a jar test apparatus (Fisher-Bioblock, France). As standardized set of stirring speeds, i.e., 200 rpm for rapid stirring and 40 rpm for slow stirring, was used for comparative purposes. The initial pH of the solution was measured and then adjusted to a fixed value (depending on the experiments) using dilute HCl or NaOH solutions (0.01–0.1 M). The homogeneous dye solution was separated into several beakers, each containing 300 mL, to which various volumes of chitosan nanoparticles solution were added.

The mixtures were then stirred at high velocity (200 rpm) for 3 min, after which the velocity was decreased to 40 rpm and maintained for 15 min. The stirring was then stopped and the experiments were performed at room temperature. Following a settling time of 2 h, the samples were collected at the top of the settling beaker (the top 1 cm of the water phase) using a syringe. The collected samples were filtered through a 1.2 mm Whatman filtration membrane (held on a filter support cartridge) and analyzed by means of UV-visible spectrophotometry (Shimadzu UV 160-A). The amount of dye retained on the membrane was negligible (less than 2%).

The quantity of dye on chitosan nano particles, q (in mg g/1 or mmol g/1), was calculated according to the following mass balance equation:

q= V(C0 - Ceq)/m,

where V is the volume of solution (L); C0 and Ceq are the initial and final dye concentrations (mg L^{-1} or mmol L^{-1}), respectively; and m (g) is the amount of chitosan nanoparticles added to the solution. The quantity of dye removed from the solution was assumed to be bound to the total amount of chitosan nano particles present.

The pH, TSS and COD of the samples was measured according to the Standard Methods for Examination of Water and Wastewater, AWWA 2005.

RESULTS AND DISCUSSIONS

Characterization Chitosan Nano Particles Nanoparticle

The FTIR Analysis

The FTIR spectra of chitosan nanoparticles are shown inf Figure 1. A characteristic band at 3449 cm^{-1} is attributed to –NH$_2$ and OH groups stretching vibration and the band for amide I at 1655 cm^{-1} is seen in the infrared spectrum chitosan

nanoparticles. Whereas in the FTIR spectra of nanoparticle chitosan nano particles the peak of 1655 cm^{-1} disappear and 2 new peaks at 1645 cm^{-1} and 1554 cm^{-1} appears. The disappearance of the band could be attributed to the linkage between the phosphoric and ammonium ions. The chitosan nano particles also showed a peak for P = O at 1155 cm^{-1}. Li Feng et al [13] a observed similar results in their study of the formation chitosan nanoparticles and chitosan nanoparticles film treated with phosphate.
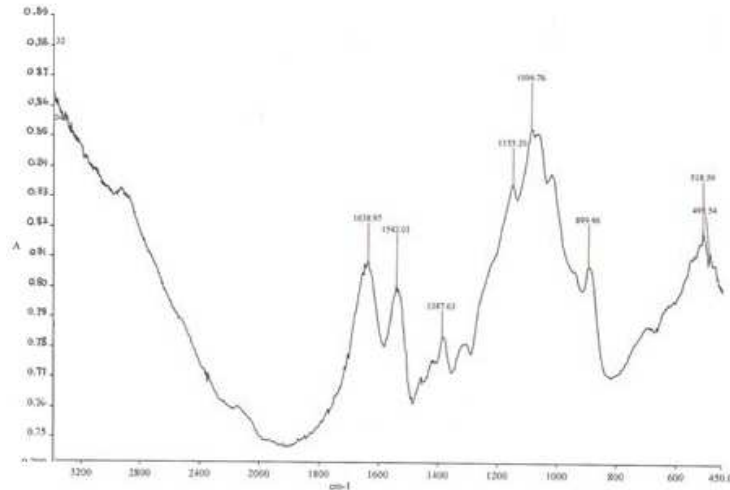

Figure 1: FTIR Spectra of Chitosan Nanoparticles

The mechanism of cross linking of chitosan nanoparticles with STPP could be either by deprotonation or ionic interaction. Chitosan nanoparticles with a pKa of 6.3 is polycationic when dissolved in acid and presents $-NH_3^+$ sites. STPP ($Na_5P_3O_{10}$) dissolved in water dissociates to give both hydroxyl and phosphoric ions. Since the cross linking of chitosan nanoparticles would be dependant on the availability of the cationic sites and the negatively charged species, it was expected that the pH of STPP would play a significant role in same. pH would bring about a change on the extent and type cross linking. Hence in the present study, pH conditions pH 8.6 were used for reaction. At pH 8.6 both OH^- and phosphoric ions were prsent and may compete each other to interact with the $-NH_3^+$ of chitosan nanoparticles.

XRD Analysis

X-ray diffraction pattern of chitosan nano particles nanoparticle are shown in Figure 2. However, no peak is found in the difractogram of chitosan nanoparticles. The XRD pf chitosan nano particles is characteristic of an amoorphous polymer. The crystal structure of the amorphous chitosan nanoparticles has been destroyed after crosslinked with sodium tripolyphosphate.
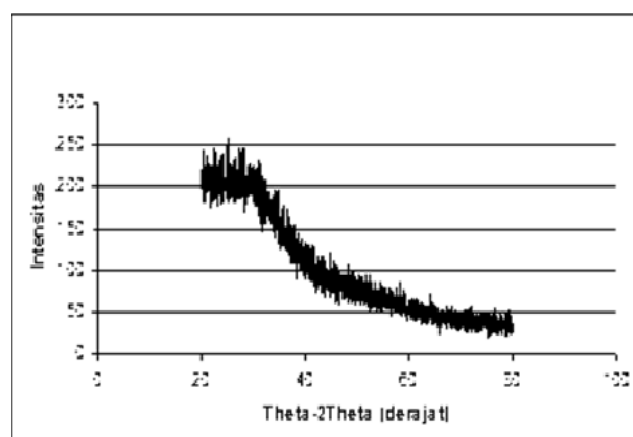

Figure 2: X-Ray Powder Diffraction Patterns of Chitosan Nanoparticles

Diameter Particle of Chitosan Nanoparticles

Figure 3 depicts the TEM image of chitosan nanoparticles along with SAED particles shown in inset. The average diameter of particles was about 23.08 -61.54 nm. Zhi et al[14] was reported, when NaOH was selected as the precipitator, the average diameter chitosan nano particles was 32-142 nm.
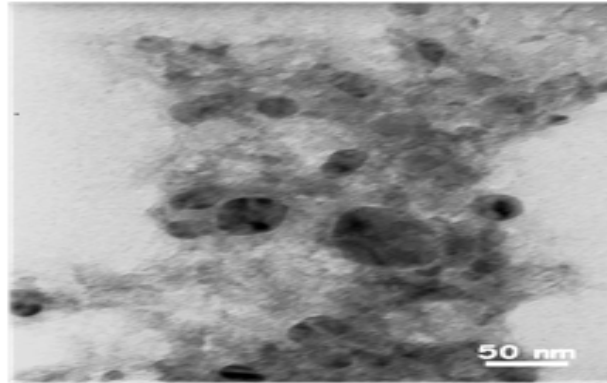

Figure 3: TEM Imagesand Size Distribution of Chitosan Nano Particles

Coagulation and Flocculation

Mechanism of Coagulation

The mechanisms of the coagulation process of acid dye on chitosan nanoparticles are likely to be the ionic interactions of the colored dye ions with the amino groups on the chitosan. In aqueous solution, the acid dye is first dissolved and the sulfonate groups of acid dye (D–SO3Na) dissociate and are converted to anionic dye ions.

$D—SO_3Na$ --------------- $D-SO3^-$ + Na+
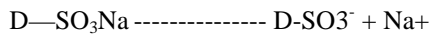
Also, in the presence of H+, the amino groups of chitosan (R-NH2) became protonated.

$R—NH_2 + H^+$ -------------- $R—NH_3^+$
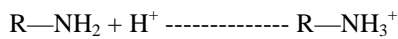
The adsorption process then proceeds due to the electrostatic attraction between these two oppositely charged ions.

$R—NH_3^+ + D-SO_3^-$ ---------------- $R—NH_3. . .O_3S-D$
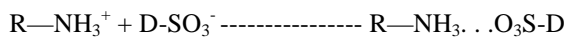
Chitosan nanoparticles has reactive amino and hydroxyl groups that interact with negatively charged surfaces. The behavior of chitosan nanoparticles involves two factors, namely hydrophobic interactions and the possibility of chain association through hydrogen bridges. The hydrophobic interactions are due to the methyl group of the acetamide function and to the –CH and –CH2 groups of the glucose ring. The H-bridges are usually generated by alcohol, amine, amide and ether functions on the chitosan nanoparticles chain. These chemical groups are implied in the competitive formation of both inter- and intramolecular H-bridges, as well as interactions with other substrates. Thus, the chemical behavior of chitosan nanoparticles varies according to the liquid media. Agata [15] report that the coagulation–flocculation of AB92 solutions prepared with demineralized water and tap water with chitosan at pH levels of 3.0, 5.0 and 7.0. The coagulation–flocculation of this dye required lower amounts of chitosan with tap water than with demineralized water. This indicates that the ionic composition of the solution, possibly sulfate, had an important effect on the sorption of AB92 by chitosan or on the configuration of chitosan at the dye–water interface. It has been previously reported that chitosan appears to have a higher MW in the presence of sulfate. Characteristics of treated waste water resulted are shown in Table 1

Table 1: Quality of Treated Wastewater

No	Before Treatement(Mg/L)	After Treatment (Mg/L)
pH	10.5-11	7.0-8.5
COD	150-450	50
TSS	80-106	25
Colour	100-250	10

The results showed that the optimum dose in using of coagulant is to use L 200 mg/l resulting TSS removal in the amount of 98% and 80% removal for COD with treated wastewater containing TSS of 25 mg/L, CODT of 50 mg/l and pH of 7.2 to 8.5.

Effect of pH on the Percentage Removal of Colour

The pH is a critical parameter in the efficiency of the coagulation– flocculation process. This parameter influences the solution properties (net charge of the dye) and the behavior of the biopolymer in the solution (charge of the amine groups). The addition of the chitosan nano particles to the dye solution changes the pH of the solution for two reasons: (a) the direct impact of the acidity of the chitosan nano particles solution, and (b) the effect of the interaction of the dye with the biopolymer. Figure 1 represents the effect of pH on colour removal. It is observed that as the pH of solution was increased, the colour removal deccreased. An extremely low of removal colour of experimental data points was obtained at pH 7, compared with the pH 5 which were adjusted to pH 5 can be explained by the above mechanism. The amino groups on the chitosan nanoparticles are not fully protonated due to insufficient H^+ concentration. As a result, there is a much smaller amount of protonated amino groups available for ionic interaction with the sulfonate groups of acid dye leading to much lower amount of dye being remove on the chitosan nano particles nano particles.
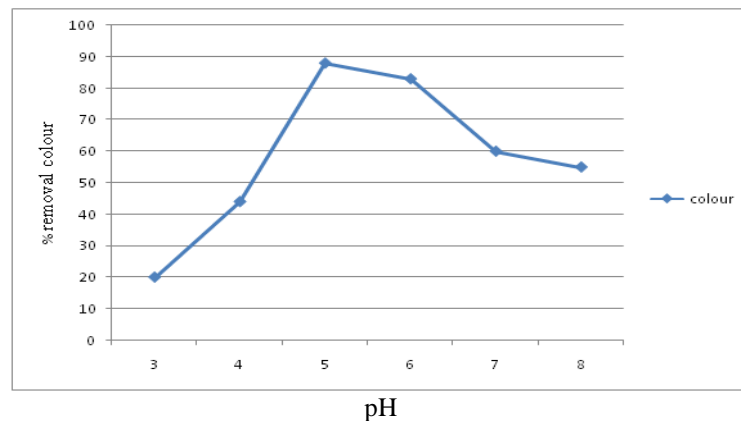
Figure 4: Effect of pH on Removal of Colour

Effect of Dosage of Chitosan Nanoparticles on Removal Colour

The chitosan nano particles dosage was varied in order to determine the best coagulant dose for each dye concentration at pH 5. As the chitosan nanoparticles dosage increased, the residual concentration of dye systematically reached a minimum before increasing again. These curves are typical of a coagulation–flocculation system controlled by a charge neutralization mechanism. The anionic dye bearing sulfonic groups is electrostatically attracted by the protonated amine groups of chitosan nano particles. This reaction neutralizes the anionic charges of dyes that can bind togetherand settle.When the protonated amine groups had completely neutralized the anionic charges, the dye removal reached itsmaximum.When the amount of chitosan nano particles added to the solution was increased, the excess protonated amine

groups restabilized the suspension and decreased the efficiency of the process [14]. The bridging mechanismis enhanced by the flocculating effect of the chitosan nano particles (due to its high MW) and by the interactions of the various anionic groups in the dye with the various protonated amine groups (inter- and intra-chain associations). Chitosan nanoparticles are involved in a dual mechanism that brings about coagulation by charge neutralization and flocculation by the bridging mechanism.

Sludge Production

In general, the amount and characteristics of the sludge produced during the coagulation–flocculation process were highly dependent on the coagulant used and on the operating conditions. In order to evaluate this parameter, the optimum chitosan nanoparticles dosage was used for experiments performed with 100 mg L$^-$ of reactive Red 120 solution at pH levels of 5.0 Once the experiment was performed in the jar test, the contents of the beakers were transferred to the Imhoff cone and the sludge production was determined by direct reading (mL of sludge produced for 500 mL of dye solution treated). Table 2 shows the results obtained using this method. Under selected conditions, the amount of sludge for both solutions was very low (12 mL of wet sludge per 500 mL of treated dye solution prepared at an initial pH of 5.0 reactive red 120 concentration: 500 mg L^{-1}; chitosan dosage: 100 mg L^{-1}).

Table 2: Sludge Reduction Under Optimum Conditions

No	Time(Min)	Sludge (Ml)
1	1	100
2	3	40
3	5	12
4	7	12
5	10	12

In the coagulation–flocculation process, the settling speed of the flocs is important, since this influences the overall cost and efficiency. Table 2 shows that considerable sludge reduction was achieved within 5 min of settling. This indicates that chitosan nanoparticles is very effective in removing dye and produces a small amount of sludge that settles very fast.

Recovery of Reactive Red 120 from Dye-Loaded Flocs

The coagulation–flocculation process generally removed the dye very efficiently: over 99% of the reactive Red 120 was transferred to flocs. The reactive Red 120 was desorbed from the dye-loaded flocs in order to regenerate the spent chitosan nano particles and economize the coagulation–flocculation process. The desorption was performed in alkaline media in order to decrease the dye's affinity for chitosan nano particles: the deprotonation of amine groups disrupts the bonds between the amine groups and the anionic groups of the dye (i.e., sulfonic functions). Table 3 shows that reactive red 120 was desorbed with sodium hydroxide (0.001–1 M) with 100% efficiency. Recovery of reactive Red 120 from dye-saturated flocs (coagulation–flocculation: initial dye concentration of 100 mg L^{-1}; pH 5; chitosan dosage of 10 mg L^{-1} ; dye recovery conditions: 30 mL of NaOH, 5 min).

The volume used for desorption studies was twenty five times smaller than that used for the coagulation–flocculation experiment. Thus, reactive Red 120 was not only effectively removed from the flocs but also concentrated. The recovered flocs were rinsed gently with water, dissolved in acetic acid solution (1%) and reused in a second coagulation–flocculation step. The efficiency of the dye removal in this step was 68%. This could be due to the loss of some flocs during their separation from the dye solution after centrifugation (by decantation).

Due to the small amount of sludge produced during coagulation–flocculation with chitosan nano particles, it was not possible to optimize the reutilization of the recovered flocs. This topic is worthy of consideration in future studies.

CONCLUSIONS

This study has demonstrated that coagulation–flocculation of reactive Red 120 with chitosan nano particles is an effective method for clarifying dye wastewater. Dye removal efficiency at various pH levels and dye concentrations was evaluated. The efficiency of coagulation–flocculation with reactive Red 120 solution was shown to be highly dependent on the pH control and coagulant dose. At higher pH levels, larger amounts of chitosan nano particles were required to reach the maximum color removal of the treated solution. Chitosan nano particles can behave as a coagulant (charge neutralization) or as a flocculant (bridging), depending on the nature of the colloids, the pH of the suspension and the experimental conditions (i.e., concentrations). The respective contributions of these mechanisms also depend on the experimental conditions and on the characteristics of chitosan nano particles (i.e., its MW and degree of deacetylation). Decreasing the pH reduces the chitosan nano particles concentration required for optimum coagulation–flocculation. The results showed a very high degree of color removal (99% at optimal conditions). The use of chitosan nano particles as a coagulant in dye wastewater treatment resulted in a very low level of sludge production. The volume of the wet sludge at the bottom of the jar test beakers after the coagulation– flocculation process was used to quantify the volume of sludge generated in the study.

Very low doses of chitosan nano particles were needed for the destabilization and sedimentation of dye solutions. The settling time was short, and very low dye concentrations were obtained within a few minutes. These observations are consistent with the commercial use of chitosan nano particles for dye wastewater treatment. It was possible to recover the chitosan nano particles from the dye-loaded flocs with 0.1 M NaOH (with a desorption efficiency of close to 100%).

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