USING CHITOSAN AS COAGULANT IN DOMESTIC WASTEWATER TREATMENT PROCESS

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Abstract: *Alternative coagulants have been considered for wastewater treatment in which chitosan may be of great interest characterized by its treatment efficiency and environmentally friendly behavior. Chitosan was very effective in removing turbidity from raw domestic wastewater at natural pH. The removal efficiency reached 81.42%, and turbidity level was 0.013 (Abs) if 4 mg Chitosan/L used in coagulation. Along with turbidity removal, total organic carbon was also removed with the removal efficiency of 37.11%. However, the capacity of chitosan coagulant in total phosphorus and total nitrogen removal was low, with the removal efficiencies were 19.61% and 10.75% respectively.*

Keywords: *Domestic wastewater treatment, chitosan, coagulant.*

1. Introduction

Domestic (also called sanitary) wastewater is wastewater discharged from residences and from commercial, institutional, and similar facilities. It is handed by wastewater treatment plans and discharged into received water bodies (rivers, sea…). General terms used to describe different degrees of treatment are preliminary, primary, secondary, and tertiary and/or advanced wastewater treatment (FAO). Conventional wastewater treatment process includes physical, chemical, and biological processes, and is aimed to remove solids, organic matter and, nutrients from wastewater.

Primary treatment is intended to remove floating and settable materials from wastewater, usually by sedimentation [11]. Primary effluent then will be further treated by to achieve required criteria for specific wastewater reuse applications or discharge to receive water bodies.

Coagulation method is widely used in water and wastewater treatments, and well known for its capability of destabilizing and aggregating colloids [2]. The coagulants commonly used are metal salts such as polyaluminum chloride (PAC) which may have several environmental consequences: an increase in metal concentration in water and production of large volume of (toxic) sludge. Alternative coagulants have been considered for

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environmental applications in which chitosan may be of great interest characterized by its treatment efficiency and environmentally friendly behavior [8]. It is effective in the removal of suspended solids and the colloid materials while nutrients still remain in the coagulated supernatant [6], [10]. Chitosan possesses many outstanding characteristics as applied in the coagulation of wastewater treatment process. It was applied in treatment of milt factory wastewater, brewery factory wastewater, surimiwash water, and many other kinds of wastewater [13], [3], [4]. It is effective in the removal of suspended solids and the colloid materials while nutrients still remain in the coagulated supernatant [12]. Thus the remained nutrients can be utilized for the aim of water reuse such as irrigation for crops or microalgae cultivation. From this point of view, we study the capacity of chitosan coagulation in domestic wastewater treatment process.

2. Materials and methods

Raw wastewater samples were collected from the Koto Domestic Wastewater Treatment Plant (Okayama city, Japan). In every sampling, wastewater was taken at the influent to the primary sedimentation tank taken from 2014, July 4^{th}until 2015, January 29^{th}. The experiment was conducted at natural pH conditions of wastewater; pH is close to 7.

Chitosan stock solution (1g/L) was prepared using commercial Chitosan (Chitosan500, 032-14412) from Wako (Japan). Chitosan powder (100mg) was dissolved in 0.1N HCl solution and then diluted to the desired concentration using distilled water.

Coagulation was carried out in a four-spindle multiple stirrer unit (Water Cohesion Reaction Tester, Miyamoto Riken Ind. Co., Ltd., Japan). Wastewaters were divided into four beakers; each containing 500mL. Each beaker was subjected to a rapid mixing step at 150rpm for 5 minutes, a slow mixing step at 50rpm for 15 minutes and then left to settle for 30 minutes. Different volumes of Chitosan were added to the beakers in the first step. All jar tests were conducted under temperature of $20^{o}C$ in an air-conditioned room. Samples were then collected in the upper part of the beakers to measure the various parameters of the treated effluents.

In order to determine the physical-chemical characteristics of the effluents and treated effluents, a large number of analyses based on Standard Methods for the Examination of Water and Wastewater (APHA, 2005) were conducted on each sample and the following parameters were measured: pH, Zeta Potential, Turbidity, Total Organic Carbon (TOC), Total Phosphorus (TP), Total Nitrogen (TN).

3. Results and discussion

Raw wastewater was taken from Koto Domestic Wastewater Treatment Plant, Okayama city, Japan. The characteristics of samples are shown in table 1.

***Table 1.** Characteristics of raw wastewater*

Parameters	Average	Range
pH	6.93	6.46 - 7.2
Turbidity (Absorbance at 660nm)	0.10	0.031 - 0.18
Zeta potential	-17.95	-20.5 - -14.1
UV254	0.60	0.131- 1.087
Total Nitrogen (mgL^{-1})	26.10	11.83 - 37.60
Total Phosphorus (mgL^{-1})	5.22	1.19 - 11.19
Total Organic Carbon (mgL^{-1})	27.38	4.724 - 47.57

3.1. Effects of chitosan coagulation on pH, turbidity, zeta potential

Over the usual range of water pH (5-9), particles, which always carry a negative surface charge and because of this, are often colloidally stable and resistant to aggregation. Coagulants are then needed to destabilize the particles. Destabilization can be brought about by either increasing the ionic strength (giving some reduction inthe zeta potential and a decreased thickness of the diffuse part of the electrical double layer) or specifically absorbing counterions to neutralize the particle charge [8].

Chitosan is widely being used because of its particular macromolecular structures with a functional group, $-NH_2$ which can interact with contaminants [6]. Chitosan remove insoluble particles and dissolved pollutants by a charge neutralization associated to bridging effect mechanisms.

In this experiment, the capacity of chitosan in suspended solid or turbidity removal was studied under different chitosan dosage at natural pH of wastewater, neutral pH.

In the range of pH around 7, chitosan coagulation decreases turbidity of domestic wastewater from 0.11 to 0.02 absorbance at 4mg/L chitosan dose. Chitosan coagulation removed 74.03% of turbidity. The pH of wastewater unchanged in coagulation process.

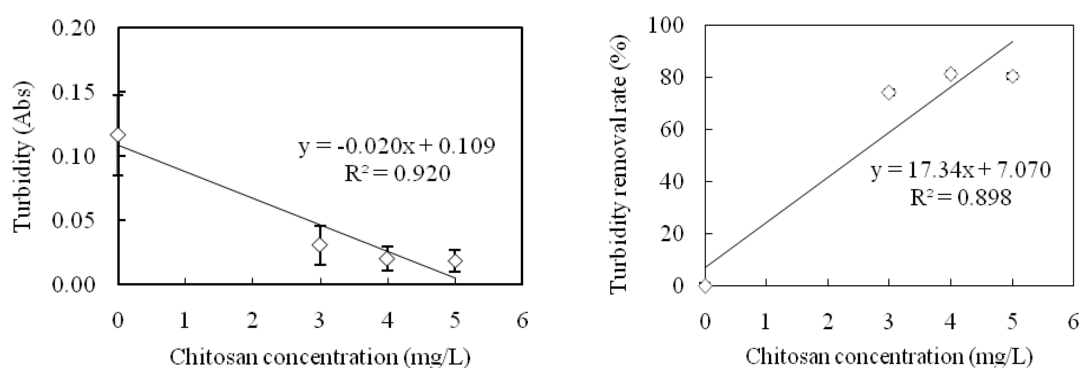

***Figure 1.** Turbidity and turbidity removal ratio of coagulated wastewater at different chitosan doses at natural pH*

The capacity of chitosan coagulation in removal turbidity depend significantly on pH of wastewater and zeta potential of colloidal particles.

The pK_a of amine groups of chitosan is close to 6.5 for fully dissociated chitosan. This means that at pH of 5.0 or less, more than 90% of the amine groups are protonated [9]. This protonation gives chitosan ability to neutralize metal anionic, organic compounds. This number of protonated amine groups decrease with the increase of solution's pH.

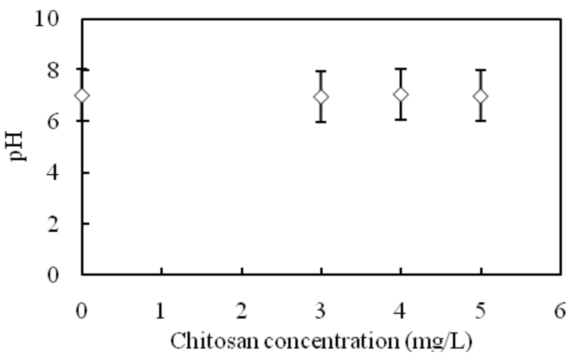

Figure 2. *pH of supernatants which coagulated at different chitosan doses*

In this study, the pH of wastewater was unaffected at different chitosan dosages. So the pH of solution did not effect on chitosan protonation, and not affect to turbidity removal of chitosan coagulation.

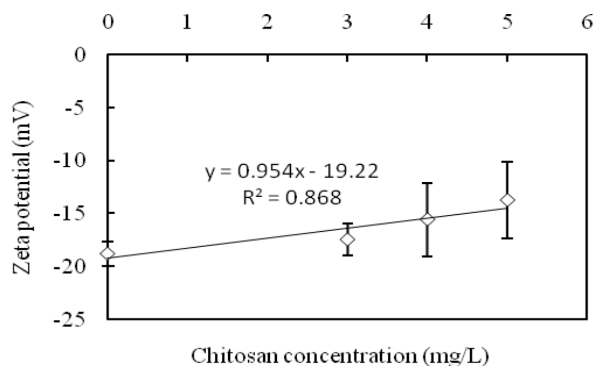

Figure 3. *Zeta potential of supernatants which coagulated at natural pH at different chitosan doses*

The zeta potential is a key indicator of the stability of colloidal dispersions. The magnitude of the zeta potential indicates the degree of electrostatic repulsion between adjacent, similarly charged particles in dispersion. Colloids with high zeta potential (negative or positive) are electrically stabilized while colloids with low zeta potentials tend to coagulate or flocculate.

In the neutral pH condition, the negative zeta potential of particles of wastewater decreases with the increasing of added positive-charged chitosan dosage. However, when the chitosan coagulation reaches the highest efficiency, 4-5mg chitosan/L dose, and the turbidity after Jar-test is lowest, the zeta potential of wastewater still does not reach the neutral point. In other words, the surface of particle still has negative charge. Chitosan as cationic polymer can destabilize the colloidal particles.

Moreover, the results shown in figure 4 point out that when chitosan dose excess optimum dose, the turbidity increases as chitosan dose increases. These results were similar to Chau's study.

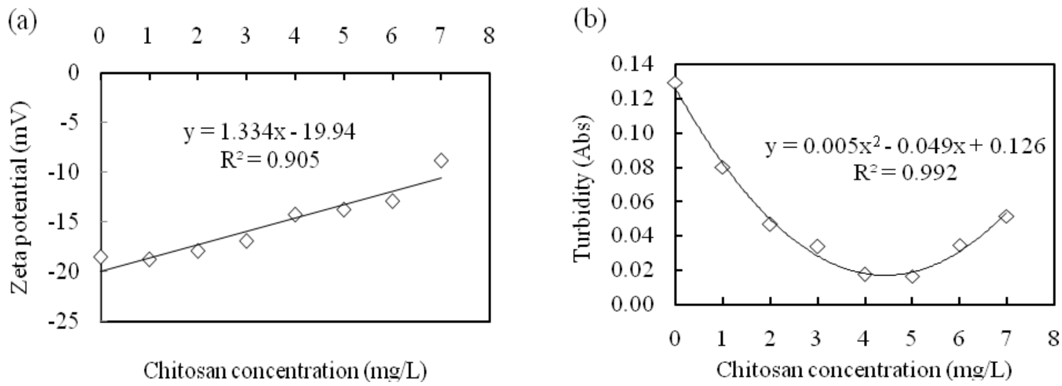

Figure 4. *The turbidity (a) and Zeta potential (b) of coagulated wastewaters at different chitosan doses at natural pH*

Those results confirm the double effect of chitosan in the process. At the neutral pH, both the coagulation (charge neutralization) and flocculation (colloid entrapment) mechanisms were involved in the removal of colloidal particles [9]. However, the major mechanism for chitosan to destabilize the colloid particles is the bridging flocculation [5].

3.2. Effect of chitosan coagulation on nutrient components

The removal of nutrients in wastewater of coagulation/flocculation may be related to removal colloidal particles process. The results of chitosan coagulation in total phosphorus removal at different chitosan doses are shown in Figure 5.

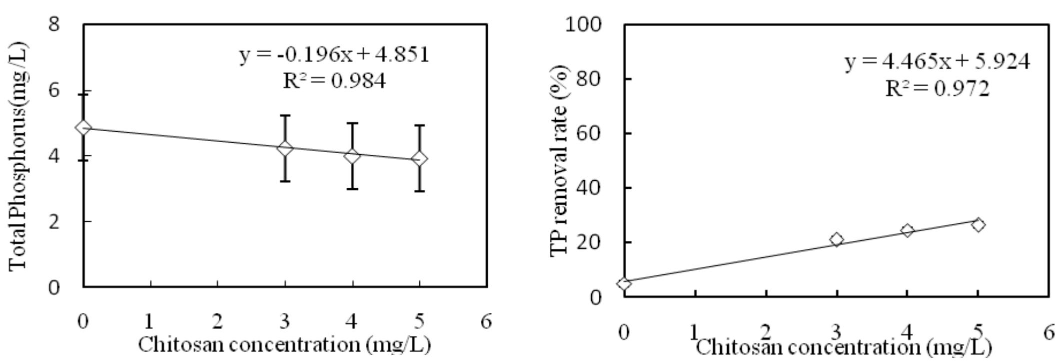

Figure 5. *Total phosphorus (a) and total phosphorous removal rate (b) of coagulated wastewater at different chitosan doses*

Phosphorus is a component which should be limited of wastewater effluent since it can cause eutrophication of surface water. In the coagulation-flocculation process, phosphorus is removed by being incorporated to solids in suspension and the reduction of these solids during the process including the removal of the phosphorus; or through the formation of phosphate precipitates with the metal salts used as coagulants [1]. In the case of chitosan coagulation, removal of phosphorus compound may be linked to the colloidal particles. Chitosan coagulation can remove 19.61% of total phosphorus and 10.75% of total nitrogen at 4mg/L of chitosan dose. Those values are rather low compare to metal-coagulants [12].

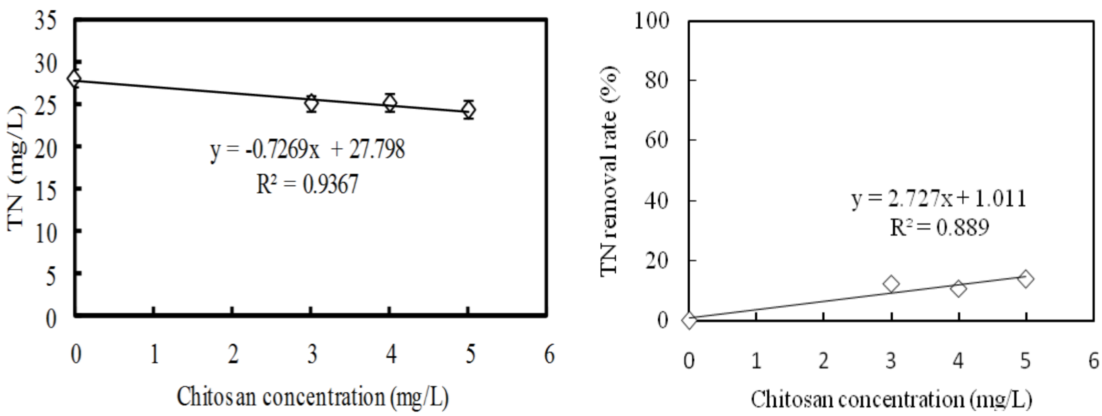

Figure 6. *Total nitrogen (a) and total nitrogen removal rate (b) of coagulated wastewater at different chitosan doses*

The compounds made of colloidal particles, which may contain nitrogen, are increasingly taken into account in water treatment processes due to the effects they may have on the environment. The nitrogen compounds in varied forms could reduce the levels of dissolved oxygen in the receiving water stimulate algae growth, assumed toxicity for some forms of water life.

The nitrogen compound in wastewater includes organic nitrogen, nitrate, nitrite and ammonium. The organic nitrogen represents nitrogen contained in natural compounds like proteins, peptides, nucleic acids, urea and a large number of synthetic organic compounds.

Nitrogen removal through the coagulation-flocculation process is related to the removal of colloidal matter [1].

3.3. Effect of chitosan coagulation on total organic carbon

The capacity of chitosan coagulation in total organic carbon removal is presented in figure 6. In this study, chitosan removed 37.13% of TOC and 38.50% of TOC at 4mg/L and 5mg/L chitosan, respectively. These results may be due to the condition of coagulation process, at pH = 7, instead of pH = 6.

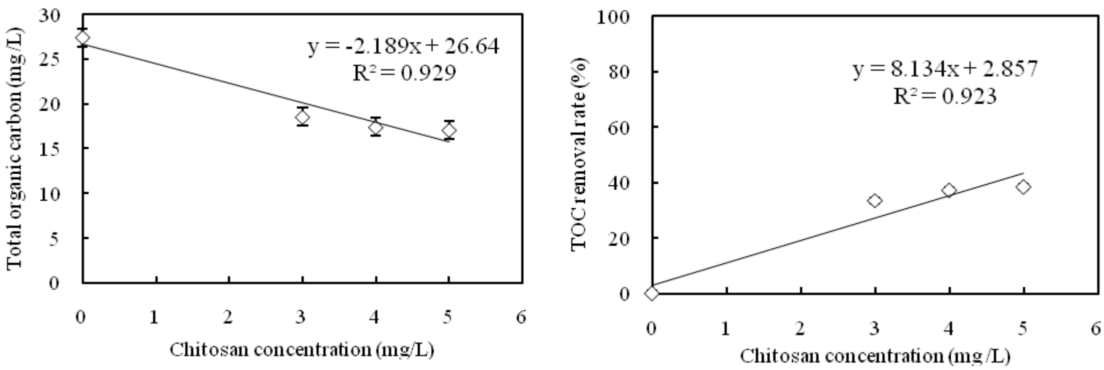

Figure 7. *Total organic carbon (a) and total organic carbon removal rate (b) in supernatant after coagulation by different chitosan doses*

The properties of wastewater after coagulation are shown in table 2.

Table 2. *Characteristics of coagulated wastewater*

Parameters	**Average**	**Range**	**Removal rate (%)**
pH	6.91	6.64 - 7.18	-
Turbidity (Absorbance at 660nm)	0.013	0.009 ≈ 0.045	81.42
Zeta potential	-15.55	-19.4 ≈ -1.61	-
UV254	0.31	0.083 ≈ 0.717	45.66
Total Nitrogen (mgL^{-1})	23.30	11.18 ≈ 36.03	10.75
Total Phosphorus (mgL^{-1})	3.76	0.56 ≈ 5.94	19.61
Total Organic Carbon (mgL^{-1})	19.12	1.83 ≈ 30.7	37.11

4. Conclusion

Chitosan is very effective in removing of turbidity when being used as coagulant in domestic wastewater treatment at natural pH. The removal efficiency reaches 81.42%, and turbidity level is 0.013 (Abs) if 4mg Chitosan L^{-1} is used in coagulation. Total organic carbon was also removed with the removal efficiency was 37.11%. However, the capacity of chitosan coagulant in total phosphorus and total nitrogen removal is low, with the removal efficiencies of 19.61% and 10.75 % respectively.

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