Utilization of chitosan clam bloodshells as a coagulant for processing electroplating waste

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Abstract. Utilization of coagulants with natural ingredients has been widely developed, the advantage of using biocoagulant is the availability of abundant material, easy to obtain it, from renewable materials, and low toxicity. This research compares chitosan clam bloodshells (Anadara granosa) coagulan and alum coagulan, to reduce concentration total chrome, nickel and turbidity in electroplating waste. The variations of coagulan, 300 mg/l and 600 mg / l, variation of the speed used is 150 rpm and 300 rpm. Results of the research, Alum can remove TSS by 93.75% at dose 300 mg / l, stirring speed of 150 rpm, Nickel by 32.49% at dose of 600 mg / l, stirring speed of 300 rpm, total Chrome removal of 64.09% at dose of 600 mg / l, stirring speed of 300 rpm. Coagulant chitosan TSS by 97.79% at dose 300 mg / l and 600 mg / l, stirring speed of 150 rpm, Nickel by 50.73% at dose of 600 mg / l, stirring speed of 150 rpm, the total chromium by 72.88% at dose of 600 mg / l, stirring speed of 150 rpm. Alum and chitosan coagulant the ability to neutralize the pH in accordance with the standard quality standard of electroplating waste, from 6.2 to 7.6.

1. Introduction
The electroplating industry is one of the industries that develops following market. To get a metallic impression on the material, a plating process using Chrome and Nickel is required. After the gilding process, washing is carried out to remove the remaining material. The content of chromium and nickel will be carried in the residual waste of production. Chrome and nickel are heavy metals that can cause toxicity when discharged into the water. For this reason, it is necessary to process them before being discharged into the environment.

The use of coagulants with natural ingredients has been developed, the advantages of using biocoagulants are abundant availability of materials, easy to obtain, from renewable materials, and low toxicity. Chitosan from shrimp shells is tried for drinking water treatment, increasing chitosan concentration affects the final water quality. The turbidity parameter can reduce up to 50%, TDS 27.16%, and electrical conductivity 48.23%. Meanwhile, microbiological parameters can be dissolved to zero [1].

The flocculation coagulation method is one of the easy and inexpensive waste treatment methods, the use of biocoagulants to reduce the turbidity concentration and TSS of domestic waste, using the Oyster Mushroom Chitin as a coagulant can reduce the turbidity concentration up to 84% while TSS can be reduced up to 96% with a dose optimal 600 mg / L with a stirring speed of 150 rpm.
Chitosan is a polymer material that has many benefits, chitosan is widely used in agriculture, food and beverages to cosmetics. In the environmental field chitosan is utilized not only for drinking water treatment, but also for wastewater treatment. Chitosan from shrimp shells is used to treat textile waste, chitosan can reduce phosphate by 60%, COD is more than 90%, chitosan can work efficiently in a freer pH range to 5.25, more flexible than commercial polymers that are efficient at pH below 4.5 [2].

Chitosan is a biomaterial, mainly produced from alkaline deacetylation (40-50% NaOH) chitin in which N-deacetylation is almost never complete. Chitosan is considered to be a partially deinetylated derivative of chitin. It is an abundant natural biopolymer obtained from a crustacean and arthropod exoskeleton which is a non-toxic copolymer consisting of \( \beta^-(1,4) -2\)-acetamido-2-deoxy-D-glucose and \( \beta^-(1,4) -2\)-anaino-2-deoxy-D-glucose unit [1]. This biopolymer offers a variety of unique applications including bioconversion for the production of value-added food products, preservation of food from microbial damage, formation of biodegradable films, recovery of waste materials from processing disposal food, water purification and clarification and acidification of fruit juices.

2. Methods

This research used a jar test, using chitosan from blood clam shells as a coagulant. The research variables consisted of independent variables, namely the chitosan concentration of 300 mg / L and 600 mg / L, the fast stirring speed of 150 rpm and 300 rpm, as a comparison, alum with the same concentration was used. Meanwhile, the dependent variable was the concentration of total chromium, nickel and TSS. As a comparison, alum with the same concentration was used. The chromium and nickel analysis method used ASS while the TSS concentration used the gravity method.

3. Results

Initial analysis was carried out to determine the concentration of electroplating waste before processing, the initial data were as follows in table 1.

| Parameter      | Result (mg/l) |
|----------------|---------------|
| Nickel (Ni)    | 20.62         |
| Total Crom (Cr-T) | 28.54        |
| TSS            | 45.25         |
| pH             | 1.2           |
| Temperature    | 30 °C         |

The results of the preliminary analysis are compared with the Quality Standards for the Governor of East Java Regulation Number 72 of 2013. The results of the initial analysis of electroplating waste concentrations exceed the predetermined quality standards, therefore it is necessary to process them before being discharged into water bodies. After conducting a preliminary analysis, research was carried out to obtain the final concentration values of TSS, Nickel (Ni) and Total Chromium (Cr-T) in electroplating waste after chemical processing with coagulation-flocculation with variations in the types of alum coagulants and blood shell chitosan, coagulant dose and stirring speed. The final concentration values for TSS, Nickel (Ni) and Total Chrome (Cr-T) can be seen in the following table 2, 3 and table 4.
Table 2. Percentage of TSS concentration removal.

| Coagulan | Coagulan Dose (mg/l) | Rapid Mixing (rpm) | Initial Concentration (mg/l) | Final Concentration (mg/l) | Percentage Removal (%) |
|----------|----------------------|--------------------|-----------------------------|---------------------------|------------------------|
| Alum     | 300                  | 150                | 45.25                       | 2.83                      | 93.75%                 |
|          | 300                  | 45.25              | 5.25                        | 88.40%                    |
|          | 600                  | 150                | 45.25                       | 3.42                      | 92.44%                 |
|          | 300                  | 45.25              | 3.67                        | 91.89%                    |
| Chitosan | 300                  | 150                | 45.25                       | 1                         | 97.79%                 |
|          | 300                  | 45.25              | 3.5                         | 92.27%                    |
|          | 600                  | 150                | 45.25                       | 1                         | 97.79%                 |
|          | 300                  | 45.25              | 5.33                        | 88.22%                    |

Table 3. Percentage of Nikel concentration removal.

| Coagulan | Coagulan Dose (mg/l) | Rapid Mixing (rpm) | Initial Concentration (mg/l) | Final Concentration (mg/l) | Percentage Removal (%) |
|----------|----------------------|--------------------|-----------------------------|---------------------------|------------------------|
| Alum     | 300                  | 150                | 20.62                       | 15.38                     | 25.41%                 |
|          | 300                  | 20.62              | 15.1                        | 26.77%                    |
|          | 600                  | 150                | 20.62                       | 14.22                     | 31.04%                 |
|          | 300                  | 20.62              | 13.92                       | 32.49%                    |
| Chitosan | 300                  | 150                | 20.62                       | 11.42                     | 44.62%                 |
|          | 300                  | 20.62              | 11.98                       | 41.90%                    |
|          | 600                  | 150                | 20.62                       | 10.16                     | 50.73%                 |
|          | 300                  | 20.62              | 10.92                       | 47.04%                    |

Table 4. Percentage of chromium concentration removal.

| Coagulan | Coagulan Dose (mg/l) | Rapid Mixing (rpm) | Initial Concentration (mg/l) | Final Concentration (mg/l) | Percentage Removal (%) |
|----------|----------------------|--------------------|-----------------------------|---------------------------|------------------------|
| Alum     | 300                  | 150                | 28.54                       | 13.09                     | 54.13%                 |
|          | 300                  | 28.54              | 12.9                        | 54.80%                    |
|          | 600                  | 150                | 28.54                       | 10.94                     | 61.67%                 |
|          | 300                  | 28.54              | 10.25                       | 64.09%                    |
| Chitosan | 300                  | 150                | 28.54                       | 11.56                     | 59.50%                 |
|          | 300                  | 28.54              | 11.72                       | 58.93%                    |
|          | 600                  | 150                | 28.54                       | 7.77                      | 72.78%                 |
|          | 300                  | 28.54              | 7.74                        | 72.88%                    |
4. Discussion

From the three test parameters, the efficiency of using chitosan as a coagulant over alum was obtained, with the results for TSS being able to set aside up to $97.79\%$, $50.73\%$ Nickel while $72.78\%$ for chromium.

Total suspended solid (TSS) is a total solid substance found in water, which can be either a biotic or an abiotic component. TSS is an important factor in water quality. Changes in the quality of TSS can cause physical, chemical and biological changes. Physical changes to water can cause reduced penetration of sunlight into water bodies. Chitosan is a biocoagulant that can reduce TSS, this is because chitosan is a multi-biological polymer, has a positive charge and contains free amine groups that provide a high ability for chemical relevance to molecules with negative charges such as protein, fat and mineral ions.

Chitosan (an amino-polysaccharide obtained from deacetylation of chitin, the main constituent of crustacean shells and insect cuticles) exhibits cationic character in acidic media which allows its dissolution, formation, and possible ion-exchange interactions with anionic compounds (properties applied to adsorption) and the coagulation-flocculation process. In neutral media, non-protonated amino groups allow the complexation of metal cations or organic chemicals in solution, these substances contribute to complex metals and their recovery by complexation-assisted ultrafiltration. It can also be used to flocculate organic compounds (as anionic dye). In the solid state, it can be used for the adsorption of metal ions, as well as the adsorption of organic compounds (dyes, pesticides, drugs, endocrine disruptors, etc.) [3].

The number of amino groups (NH2) along the chitosan chain, helps create cationic sites along the chitosan polymer due to their deprotonation when dissolved in water near neutral pH. Positively charged sites on the polymer can attach to negatively charged colloids, resulting in coagulation. Because higher DD results in higher positive charge on the polymer, higher reduction of bentonite and kaolinite would be expected from higher DD chitosans [4].

The percentage of TSS that can be removed can reach $97.79\%$, this is due to the high content of amine groups in chitin which provides a cationic charge at acidic pH and can destabilize colloid suspensions to form floc nuclei. Chitin is a long-chain polymer with a positive charge at the pH of natural water, while colloidal material is negatively charged with the help of stirring, destabilization of colloidal particles will occur. Furthermore, there will be neutralization or reducing the negative linkages in the particles so that it is possible to have van der waals forces to encourage colloid agragmentation and fine suspended substances to form microfloc [5].

In addition to the dose of chitosan 300 mg / l, the optimal TSS concentration decreased, when compared to the 600 mg / l dose, high doses allow more reactions to occur. However, the formation of flocculent particles did not run perfectly. This can be seen from the percentage of TSS that can be removed.

The use of chitosan as a coagulant is more effective when compared to alum, at the same dose the percentage of TSS for alum is $93.74\%$, while for chitosan it can reach $97.79\%$, this shows that chitosan coagulant is one of the reliable biocoagulants and has the same ability with chemical coagulants.

In chitosan with foculan, zeta potential values increased as coagulant dose increased. Neutralization played a role in particle removal from humus effluent. Flocolan is composed of polymeric chains that adorn into the surface of particles, because of interaction such as Coulombic, dipole, Van der Walls or hydrogem bonding. These interactions may occur at different points along the chain. Additionally, these chains extend and attach on to other particles which results in bridging between particles. Known as inter-particle bridging, this mechanism is widely recognised as the main process for particle removal by biopolymers [6].

The amino groups presented in chitosan also make good chelating ligands that are able to firmly bind various metal cations, and the lone pairs on the nitrogen atom and the oxygen atom are donated to the metal ion to form coordination bonds, since several amino groups and hydroxyl groups are present on the chain. long polymeric, the chain can wrap around metal ions and adopt a configuration such as several amino groups bonded to a metal atom at the same time; this type of class leads to the formation
of highly stable metal complexes, and this property makes them useful for the concentration of radioactive metal removal and other hazardous heavy metal contaminants [7].

Compared with the effect of chitosan dose and pH, mixing time plays an important role in floc formation and growth in the flocculation process. The polymer flocculants are scattered throughout the media and adsorbed on the surface of the colloid particles for bridging between particles or neutralization of charges during the mixing period. In addition, longer mixing times will increase floc breakage. Hence, it decreases the flocculation rate. On the other hand, if the mixing time is too short, the collision between the flocculant and the colloid is not efficient at settling the suspended solid in the wastewater. Thus, the flocculation rate is not optimal in this condition. Therefore, a research was conducted on the effect of mixing time in flocculation [8]. In the flocculation cogulation process the separation process involves the formation of clumps of particle rays, which depend on the stirring process. The use of chitosan in batik waste can reduce COD by 71.69%. in other waste COD get the same results, this shows that chitosan can be used as a biocoagulant [9]. Chitosan is used for textile waste treatment, the results showed that pH affects the processing process. A high percentage of pH 5 occurs, this is due adsorption can be affected by the presence of lots of –NH2 groups of chitosan, causing interactions with carboxyls the pectin group decreased. This resulted in an increase the number of -COO groups in pectin, which can interact with methylene blue. Moreover, it is assumed that chitosan-pectin and membrane pores Pec-Chi-BADGE match, which results in an even greater methylene blue adsorption [10].

The total Ni removal efficiency by CAC and CPCTS-g-P (AM-AMPS) was 99.3% and 99.4%, respectively. Two-stage flocculation with CPCTS-based flocculants can reduce the total Cr and Ni concentrations to 1.0mg / L and 0.5mg / L. The relationship of removal capacity and structural properties between flocculants with different functional groups was determined by Fourier transform infrared spectroscopy, core magnetic resonance, microscopy, scanning electrons, and X-ray diffraction. The micro-interface behavior between colloidal particles and solution during integrated chelation-flocculation is described. Thus, CPCTS-based flocculants can be a potential material for removing high amounts of Cr and Ni ions in industrial wastewater [11].

Chitosan possesses a cationic character in acidic medium enabling its dissolution and possibilities of ion-exchange interactions with anionic compounds. This offers the probability of acting as a sequestrant and can also undergo chemical modifications yielding a large variety of useful derivatives. In this research work, chitosan was dissolved using acetic acid at different concentrations to observe the effect of chitosan dosage in textile effluent parameters obtained from a local factory. Results revealed that chitosan could successfully be used to coagulate and flocculate anionic suspended solids to lower down the TDS, COD, BOD values and more effectively used as a bio-adsorbent to remove color from the wastewater. The highest chitosan performance was obtained with 60ml of 0.05% and 0.1% chitosan solution which reduced the polluted water characteristics like COD, BOD, and TDS below the maximum discharge value with a significant reduction in color [12].

5. Conclusion

• Chitosan can be use as a biocoagulant to replace chemical coagulant.
• Chitosan is more effective to remove TSS, Chrome and Nickel in electroplating waste.
• The final result of coagulation flocculation for the three parameters not yet eligible for disposal.
• Coagulation flocculation is a preliminary treatment, it needs advanced processing.

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