Natural Flocculant VS Chemical Flocculant Where Is Better To Used In Wastewater Treatment

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Abstract. Nowadays, Coagulation-flocculation process is still common method were used in both large and small scale in wastewater treatment. It’s process an effective method as pretreatment. Flocculant (natural aid) can use many material is an important factors for coagulation-flocculation process. Many materials were used for coagulant-flocculant aid, but typically can be divided into chemical, grafted and or natural aid. Chemical flocculant was made from monomers formed to electrolytes polymers, that is cationic polymers, anionic polymers or non-ionic polymers, such as polyacrylamide have been widely used for decades. Grafted flocculants were synthesized by combining the properties of polymers, both synthetic and natural by ‘connect to’ method, such as Polydiallyldimethylammonium chloride (polyDADMAC or polyDDA). Whereas natural flocculant can be derived from seed of plantago, ovata, moringa, oliferia, etc. Some natural starch can be used as natural aid also. The main advantages of natural flocculant are their renewability, biodegradability, nontoxicity and relative costeffectiveness. but for development in the future constrained by some challanges, Natural flocculant tend to have shorter live which caused by biodegradability of active component, floc will loose. Besides that, chemical flocculants are used because of their easy use. However, in many studies, the usage of chemical flocculant will have an important environmental impact, such as, producing toxic sludge containing metal hydroxides which causes problems with their disposal and increasing metal concentrations (eg aluminum) which can have an impact on the sustainability of human health. This paper will review some chemical flocculant and natural flocculant also tell about environmental affect, both disadvantages and potential which is better used to wastewater treatment.

1. Introduction

Various types of industries that produce waste water in it contained dissolved solids, suspended solids, organic and inorganic particles, impurities and metals. The function of the very small size and charge on its surface is to attract other particles closer and form a heavier masses for precipitation and filtering [1] Therefore, colloidal particles in wastewater are important to be degraded with the right method and this is very important to note. [2] Coagulation / flocculation is a process of separating substances, whether solid or liquid, which functions to remove solids, both suspended solids and dissolved solids, organic matter as well as colloids in wastewater.. [3] This process takes place after the addition of coagulant and / or flocculant, soft particles will be scattered and collected or agglomerated to form larger particles (clots) then settles and causes clarification of the system. By this time, flocculation is generally carried out by the addition of chemical flocculants such as electrolyte polymers and / or oil-based flocculants, such as polyacrylamide and polyethyleneimine. [4] Cheaper price and its easy to use to make chemical flocculants are often used in the flocculation process. However, if the use of the dose is low they will not clump efficiently, and if the use of the dose is high it can leave metals from wastewater treatment, such as aluminum hydroxide, which can cause Alzheimer's disease. [5] Also, toxic sludge (metal hydroxide) is produced which is difficult to dry, expensive to process, and cannot be reused for soil in agriculture. [4] Natural flocculants attract much attention as an alternative to wastewater treatment and as a substitute for synthetic oil-based flocculants because of their environmentally friendly. [3] They attract a lot of
attention because they are considered safe in their usage, resistant to biological degradation, produce organic sludge degraded by microbes, and can be reused in agricultural soils as fertility enhancers. [4,6] Also, the advantages of natural flocculant are their renewability, nontoxicity and relative costeffectiveness. [7] Some natural flocculant was derived from plant such as from Cassava starch, Moringa oleifera seed, Plantago ovata seed, Cassia obtusifolia seed, Surjana seed, Maize seed, Tamarindus indica seed, Jatropha curcas seed, Strychnos potatorum nut, extracted pandan leaves, Corn flour and durio starch etc. [8] Generally, the clarification process by natural flocculant with three steps, primary processing to eliminate unwanted parts, this process is carried out by manual or mechanical pulverizing. The next step is secondary processing (extraction) where this process is used organic solution or alcohol, water or salt for extraction. Third, the process is tertiary processing (Purification) by dialysis, lyophilization, ion exchange or precipitation. [9] Natural flocculant tend to have shorter live which caused by biodegradability of active component, floc will loose. In the process of flocculation, flocculants have an important role in them, in many studies of flocculation, high efficiency and efficient search for flocculants is a challenge going forward. The main variables measured to validate flocculation efficiency include floc deposition rate, sludge volume index (SVI), percent of solids resolved, supernatant turbidity or clarity, percentage of pollutant release or water recovery depending on industrial application. [13] The output variables are all manifestations of the floc or aggregate size distribution, the shape and structure of the floc produced during the flocculation process. Larger, stronger and denser flocks are good for sedimentation, easy to filter, and high clarification process.

2. Chemical Flocculant
Some types of chemical flocculants that are often used in the flocculation process are polynatriumacrylate, polyacrylamide, copolymers of acrylamide and N,N − dimethyl amino propylene acrylate. Mainly because of their low prices, where their market prices are much lower compared to chemical flocculants as shown in Table 1.

| Chemical materials Price, €/tonne | Coagulants | Cationic flocculants | Anionic flocculants |
|-----------------------------------|------------|---------------------|--------------------|
| Lime                             | FeCl3      | FO-4700             | FO-4490            |
| 130                              | 450        | 2980                | 2800               |
| FLOCAN                            | AN 934     |                     |                    |
| 2500                             | 2550       |                     |                    |

Nevertheless, in many studies, the usage of chemical flocculant will have an important environmental impact, such as, producing toxic sludge containing metal hydroxides which causes problems with their disposal and increasing metal concentrations (eg aluminum) which can have an impact on the sustainability of human health. [10] Other weakness include large amounts of flocculation efficiency, are very sensitive to pH, are not efficient at very fine particles, are inefficient in cold water (eg polyaluminium chloride) and only apply to some dispersion systems [1]. In order to minimize the weakness of chemical flocculants, many factors have been considered to find alternatives and reduce the dose of harmful chemical flocculants.

3. Natural Flocculant
Recent years, specialization in environmentally friendly materials has continued to increase in water and wastewater treatment; The discovery of natural flocculants can be an alternative to replace chemical flocculants. Natural flocculants derived from polysaccharides or natural polymers are very attractive because of the behavior of natural and environmentally friendly products. Compared to chemical flocculants, natural flocculants are safe and stable shear polymers that are sufficiently biodegradable, easy availability of reproducible resources and does not produce side effects from the waste produced. [11] In addition, as a biodegradable biopolymer, sludge can be treated properly by microorganisms. [3] Therefore, they have to be applied not only in food, fermentation, pharmaceuticals, but also in water and wastewater treatment. Colloidal particle balance can be disrupted by natural flocculants which has the potential to increase ionic strength and potentially reduce zeta, which results in diffuse thickness which can reduce parts of
the electric double layer. Also, natural flocculants contain macromolecular structures with more than one functional group (for example carboxyl and hydroxyl groups) that can attract contaminants those function to absorb by neutralizing the charge of particles. [12] A summary of its application between natural flocculants and chemical flocculants in various types of wastewater is presented in Table 2.

| Categories of flocculant | Floculant(s) | Type of wastewater | Results | Reference |
|--------------------------|--------------|---------------------|---------|-----------|
| **Chemical Flocculant**  | Neutral (N200), two cationic (K1370 and K506) and an anionic (A321) polyelectrolytes | Sanitary landfill Leachates | COD: About 80% removal; Colour: About 100% removal | [14] |
|                          | Anionic polyacrylamide | Abattoir wastewater | COD: 94% removal | [15] |
|                          | Anionic polyacrylamide (Actipol A-401) | Wastewater from sauce manufacturing plant | COD: 82% removal | [16] |
| **Natural Flocculant**   | Chitosan | Pulp and paper mill wastewater | Turbidity: 10–1.1NTU; COD: 1303–516 mg/L | [17] |
|                          | Anionic tannin | Ink-containing effluent from cardboard box-making factory | Colour: >99% removal; COD: 84% removal | [18] |
|                          | Neutral Fenugreek mucilage (Trigonella foenum-graecum) | Tannery effluent | TSS: 55% removal | [19] |

4. Conclusion and Future Perspectives
As presented above, this paper provides a point of view on the comparison of flocculation between conventional chemical flocculants and natural flocculants. Steps to choose the use of flocculants. Cationic flocculants were chosen because the surface charge of the colloidal suspension is generally negative. Cationic flocculants are usually united with non-ionic or anionic flocculants in coagulation-flocculation. On the other hand, cationic or anionic flocculants are chosen for direct flocculation. On the market, various types of flocculants are available with different molecular weights and charge densities. High molecular weight fociulants are often more desirable because they relate to a stronger connecting mechanism compared to other flocculation mechanisms.

The potential application of natural flocculants in wastewater treatment has been carried out and verified well. Natural flocculants show good results in the reduction and elimination of environmentally related parameters such as TSS, turbidity, COD and color with more than 90% removal carried out in several studies. Although many flocculation materials have been developed and
are used successfully in removing pollutants from wastewater on a laboratory scale, performance in these flocculation materials still needs to be improved in removing dissolved and suspended impurities, color molecules or dyes, heavy metals, organic or inorganic pollutants to meet environmental regulations before the waste water is discharged into the body of water. Consideration of the industry's dependence on cost-effective flocculation technology for wastewater treatment, continued research is needed so that flocculants are able to produce very significant removal efficiencies in removing pollutants even at pH and variations in other wastewater contaminants.

One way to optimize flocculation using chemical flocculants is to select or control the polymer charge density and molecular weight range. The difference in charge density and molecular weight results in different flocculation mechanisms (neutralization or bridging). Future studies must investigate how the flocculation performance influences molecular weight and charge density distribution so that it can get the right flocculant for its application. These factors can be optimized in order to reduce chemical costs and increase maintenance efficiency.

All in all, the selected flocculant has high removal efficiency so that it can eliminate or reduce any contaminants in wastewater. An environmentally friendly natural flocculant can later be reproduced with biological processes, economical cost, resulting in high removal efficiency and based on a performance and cost perspective, natural flocculants can be used as an alternative application of promising materials in the flocculation process. Everything goes back to what kind of treatment we want so we can decide on the suitable flocculant character used in the wastewater treatment process.

5. References
[1] Bratby, J., 2006. Coagulation and Flocculation in Water and Wastewater Treatment, 2nd ed. IWA Publishing, London.
[2] Divakaran, R., Sivasankara Pillai, V.N., 2001. Flocculation of Kaolinite Suspensions in Water by Chitosan. Water Res. 35, 3904–3908.
[3] Renault, F., Sancey, B., Charles, J., Morin-Crini, N., Badot, P.-M., Winterton, P., Crini, G., 2009. Chitosan flocculation of Cardboard-Mill Secondary Biological Wastewater. Chem. Eng. J. 155, 775–783.
[4] C.S. Lee, J. Robinson, M.F. Chong, 2014. A Review on Application of Flocculants in Wastewater Treatment, Process Saf. Environ. Prot. 92, 489–508.
[5] S.C. Bondy, 2016. Low Levels of Aluminum Can Lead to Behavioral and Morphological Changes Associated with Alzheimer's Disease and Age-Related Neurodegeneration, Neurotoxicology 52, 222–229.
[6] H. Salehizadeh, N. Yan, 2014. Recent Advances In Extracellular Biopolymer Flocculants, Biotechnol. Adv. 32, 1506–1522
[7] Sillanp, M., Neibi, M., C., Matilainen, A., Vepsalainen, M., 2018. Removal of Natural Organic Matter in Drinking Water Treatment by Coagulation: A Comprehensive Review. Chemosphere 190, 54–71.
[8] Zaman, Badrus, 2018. Potential of Natural Flocculant in Coagulation-Flocculation Wastewater Treatment Process. Semarang. Diponegoro University.
[9] Yin, C.Y., 2010. Emerging Usage of Plant-Based Coagulants for Water and Wastewater Treatment. Process Biochem. 45, 1437-1444.
[10] Ward, R.J.S., McCrohan, C.R., White, K.N., 2006. Influence of Aqueous Aluminium on The Immune System of The Freshwater Crayfish Pacifastacus Leniusculus. Aquat. Toxicol. 77, 222–228.
[11] Bolto, B., Gregory, J., 2007. Organic Polyelectrolytes in Water Treatment. Water Res. 41, 2301–2324.
[12] Özacar, M., S engil, I.A., 2003. Evaluation of Tannin Biopolymer as a Coagulant Aid for Coagulation of Colloidal Particles. Colloids Surf. A: Physicochem. Eng. Aspects 229, 85–96.
[13] Bohuslav Dobias, H.S., 2005. Coagulation and Flocculation, 2nd ed. CRC Press, Taylor & Francis Group, United States of America.
[14] Tatsi, A.A., Zouboulis, A.I., Matis, K.A., Samaras, P., 2003. Coagulation-flocculation Pretreatment of Sanitary Landfillleachates. Chemosphere 53, 737–744.
[15] Amuda, O.S., Alade, A., 2006. Coagulation/Flocculation Process Inthe Treatment of Abattoir Wastewater. Desalination 196, 22–31.
[16] Martín, M.A., González, I., Berrios, M., Siles, J.A., Martín, A., 2011. Optimization of Coagulation–Flocculation Process for Wastewater Derived from Sauce Manufacturing Using Factorial design of Experiments. Chem. Eng. J. 172, 771–782.

[17] Rodrigues, A.C., Boroski, M., Shimada, N.S., Garcia, J.C., Nozaki, J., Hioka, N., 2008. Treatment of Paper Pulp and Paper Millwastewater by Coagulation–Flocculation Followed By heterogeneous Photocatalysis. J. Photochem. Photobiol. A:Chem. 194, 1–10.

[18] Roussy, J., Chastellan, P., Vooren, M.V., Guibal, E., 2005. Treatment of Ink-Containing Wastewater by Coagulation/Flocculation using Biopolymers. Water SA Manuscript 31, 369–376.

[19] Mishra, A., Yadav, A., Agarwal, M., Bajpai, M., 2004. Fenugreekmucilage for Solid Removal from Tannery Effluent. React. Funct. Polym. 59, 99–104.

[20] Sarika, R., Kalogerakis, N., Mantzavinos, D., 2005. Treatment of olive mill effluents: Part II. Complete removal of solids by direct flocculation with poly-electrolytes. Environ. Int. 31, 297–304.