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Chemical coagulation and biological techniques for wastewater treatment

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Abstract. This paper reports the effectiveness of chemical coagulation and biological techniques for the treatment of wastewater from industrial and agricultural operations. Agricultural husbandry has been reported to produce wastewater that has high content of chemical oxygen demand (COD), biological oxygen demand (BOD), turbidity as well as organic and inorganic pollutants. A comparison on the use of organic and inorganic based coagulants as well as the optimum conditions required for high percentage removal efficiency of pollutants from wastewater has been reviewed. At optimum experimental condition, ferric chloride coagulants were reported to yield 98, 95, 93 and 50 % removal of color, turbidity, iron and manganese. Moreover, chemical coagulation, electrocoagulation and biological methods have been reported to display a close range in their capacities for removing pollutants from wastewater. However, biological method was observed to be highly effective in the removal of pollutants from wastewater but requires more time and produces lesser volume of sludge, when compared to chemical method in the treatment of wastewater.

Keywords: wastewater; coagulation; removal efficiency; pollutants; sludge; biological techniques; electrocoagulation.

1. Introduction

The need for high quality water resources for domestic and industrial uses and the compatibility with recirculation and reuse of wastewater are of a vital significance. There have been previous findings on the pollution of aquatic system due to pollutant run off and assimilation into the receiving water bodies [1-4]. For the continued industrial growth and increasing long term sustainability of portable water resources in addition to the requirement of a continuous supply of clean water as well as the release of clean water into the environment. There is an uttermost need to develop an economically feasible technology for the treatment of wastewater in order to create a water recirculation system for industrial operations so as to improve the efficiency of water usage and to minimize the discharge of pollutants into public water resources [5-10].

There has been a tremendous increase in the quantity of agricultural products and wastewater generated by the agricultural industries; this increase in the quantity of agricultural food products and wastewater generated has resulted from the explosion in the world population and the high demand for potable water in various part of the world [11, 12]. The development of an efficient and economically feasible wastewater treatment technology in the aquaculture industry for the recycling and reuse of both water and nutrients are paramount requirements for dealing with environmental issues, rural development, long term sustainability of water resources [9, 10, 13].

An efficient water recirculation system is of a paramount importance due to the continuing growth of the human population and increasing level of urbanization that threaten the availability of clean water for domestic and industrial activities. The concerns over drought, clean water availability and protection of the aquatic environments from pollutants continues to pose a major challenge to the ecosystem, researchers, and the general human population. This has led to a global concern on the impact of non-point source pollution on the quality of aquatic systems by agriculture activities and the need to develop a low-cost effective recirculation system for wastewater treatment [12, 14].

2. Chemical and biological techniques for wastewater treatment

2.1. Chemical treatment methods - coagulation/ flocculation method

2.1.1. Conventional and pre-polymerized metal based coagulants. The most used conventional inorganic coagulants are aluminum sulfate $(Al_2(SO_4)_3)$, ferric sulfate $(Fe_2(SO_4)_3)$ and ferric chloride $(FeCl_3)$. In order to increase the effectiveness of inorganic coagulants in water and wastewater treatment, pre-polymerized metal based coagulants such as poly aluminum chloride, poly ferric sulfate, poly ferric chloride, poly aluminum silica sulfate, and poly aluminum ferric sulfate have been developed [15].

There has been reported that $FeCl_3$ is an efficient coagulant in the removal of certain heavy metals such zinc, iron and chromium from wastewater, the amount of sludge generated when ferric chloride was used as a primary coagulant was voluminous and compacted. The addition of coagulant aid such as non-ionic polyacrylamide at various dosages enhances the

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coagulation efficiency of ferric chloride and there is a high reduction in the volume of sludge produced. Therefore the combination of FeCl₃ and coagulant aid at different ratio achieve a better removal efficiency of heavy metals from wastewater and less volume of sludge is produce during the process of coagulation and flocculation [16].

Ferric chloride as proved to be an effective coagulant by demonstrating a removal efficiency higher than 98% for color, 95% for turbidity and 93% for iron and a manganese removal efficiency of 50% when a coagulant dosages of 15 mg/L (pH 6.3) and 30 mg/L (pH 5.8) were applied. An adequate coagulation condition of 15 mg/L and a pH value of 6.3 using FeCl₃ as a primary coagulant can promote a removal efficiency higher than 95% for removing organic-iron compound from wastewater [17].

Ferric salt is less effective in removing complex of iron-organic substances due to Fe³⁺ ion reaction or the hydrolysis of the iron (III) salt strong interaction with the organic substance and the value of pH range of 4 to 5 plays a vital role in the removal of pollutants from wastewater [18]. $Fe_2(SO_4)_3$ has been reported to have a low efficiency in removing iron compounds and organic substances, and at the same time in decreasing the intensity of the color and turbidity resulting from iron and other pollutants in the groundwater [18]. It has been reported that iron coagulants has a higher performance efficiency than magnesium coagulants in the removal efficiency of arsenic (III) and (V) from aqueous arsenic spiked sample, and it was observed that background ionic species such as Cl⁻ and NO₃⁻ has no effective on the removal efficiency of arsenic while SO4²⁻ has a pronounce lowering effect on the removal efficiency of arsenic [19-21]. Both $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ have be confirmed to have a high efficiency in the removal of total dissolved solids, chemical oxygen demand (COD), biological oxygen demand (BOD) and turbidity but ferric chloride has a higher efficiency than aluminum sulfate in the removal of both nitrate and total organic carbon from wastewater [21-23].

Poly aluminum chloride has been confirmed to have a higher efficiency than aluminum sulfate and aluminum chloride in the removal of iron-organic substances, color, COD, turbidity, manganese and total organic compound from water, and the highest concentration of aluminum residue was found in the water sample subjected to aluminum sulfate treatment. A greater efficiency in the removal of iron-organic compounds, turbidity, color, and organic matter was observed when potassium permanganate was used as an oxidizing agent to aid the coagulation process. Poly aluminum chloride has shown to be one of the best considerable alternatives for aluminum sulfate, and aluminum chloride, this is due to its advantages of lesser optimum dosage, high coagulation efficiency and lesser sludge generation, nevertheless poly aluminum chloride has the disadvantage of higher cost than aluminum sulfate [24-26]. Pre-polymerized inorganic coagulants as well as nanocomposite coagulant-flocculants such as ironsilicon and aluminum-silicon flocculants-coagulants have been shown to have a high efficiency in the removal of phosphate, ammonia nitrogen, heavy metals, turbidity, color, odor, pathogens, COD, endocrine

disruptive compounds (EDC) and organic matter from water and wastewater. Composite coagulants such as iron-aluminum coagulant was found to have the highest coagulation efficiency when compared to ferric chloride and aluminum sulfate coagulants in terms of duration and temperature of the coagulation process, aluminum sulfate and poly aluminum chloride as primary coagulants has proved to be efficient in the removal of endocrine disruptive compounds such a nonyl-phenol and bisphenol A in water and wastewater [15, 27-33].

At optimum dose, zirconium-based coagulants has the highest dissolved organic carbon percentage removal than titanium and aluminum based coagulants but higher doses of Ti and Zr based coagulants are required to achieve good performances for reservoirwater treatment, compared with aluminum sulfate. Titanium based coagulants performs better than ironbased coagulants in the removal of turbidity, heavy metal and color from water and wastewater, however iron based coagulants. Titanium based coagulants formed large and heterogeneous size flocs while ferric chloride was found to have the highest sludge settling rate but also produced the largest sludge quantities [34, 35].

2.1.2. Organic polymeric coagulants

Chitosan. Chitosan is a biopolymer which is made up of a linear copolymer of D-glucosamine and N- acetyl-dglucosamine prepared by the deacetylation of chitin, which is the second most abundant biopolymer obtained from marine crustaceans, shrimps and crabs. The presence of amine functional group (acid-base properties, solubility and cationicity), degree of deacetylation and molecular weight influences the properties of chitosan to bind cationic and anionic species in near neutral and acidic solution. It has been proved that the performance of chitosan is highly dependent on the dosage of the coagulant used, the percentage removal of COD and turbidity were observed to be 99.2 and 97.2 % respectively at an optimum dosage of 5 mg/L, while the percentage removal of total suspended solids was 99.2 % at a dosage of 10 mg/L and 80 % for color removal efficiency at an optimum dosage [36-38].

Gastropod shell (GS). GS was also observed to be effective in the removal of dissolve solids, suspended solid and total solids, it was also noted that the concentration of nitrate reduced from a value of 12.8 mg/L in the 1st day to a value of 7.9 mg/L in the 30th day, in a similar manner the value of COD was reduced from 80 mg/L to 33 mg/L in the 30th day. GS has also been effective in defluorination of groundwater [39, 40]. The use of Al₂(SO₄)₃ as a primary coagulant and snail shell as a coagulant aid in the treatment of malachite green dye and aniline blue dye contaminated wastewater has revealed that the use of aluminum sulfate unaided has no coagulating effect on the malachite green wastewater but the use of snail shell reduce the aqua dye concentration. The use of aluminum sulfate and snail shell combination substantially increase the amount of malachite green dye remove from the dye wastewater, and a sludge of better settleability was obtained compared to the sludge obtain when either aluminum sulfate or snail shell was used unaided. A similar result was also obtained for aniline blue dye wastewater [41].

Poly dimethyl-diallylammonium chloride (PDADMAC) and polyamines coagulants. PDADMAC and polyamines have been reported to require a lower dose compared to inorganic coagulants (aluminum sulfate, poly aluminum chloride, ferric chloride and poly ferric sulfate), and their color, suspended solids, total nitrogen, total phosphorus, phosphate and turbidity removal efficiency is practically insensitive to pH and good results were obtained at a pH range of 3 to 10 [42]. The use of PDADMAC as a coagulating aid by coupling it with inorganic coagulants lead to a great improvement in the coagulation efficiency of inorganic coagulants, this indicate that the use of coagulation formulation is far superior to using individual coagulants in wastewater treatment. This is because the advantages of both organic and inorganic coagulants are incorporated in the formulated coagulant [42]. A comparative study on the use of PDADMAC as a coagulant aid in the coagulation behavior of aluminum based coagulants in coagulationultra filtration hybrid process has been investigated. It was noted that the coagulant aid could increase the purification performance of the coagulation-ultra filtration hybrid process, especially at low coagulant doses (1-3 mg/L) and the synergistic effect of aluminum sulfate and the coagulant aid was more significant than that of poly aluminum chloride and the coagulant aid. It was also observed the floccule sizes and compact degrees which had an opposite influence on the subsequent ultra-filtration process were improved by the use of PDADMAC as a coagulant aid [43].

Moringa oleifera (MO). A comparative study on the use of MO and polyacrylamide (PAM) as coagulant aids for poly aluminum chloride (PAC) has been successfully conducted, it was observed that MO is less effective than PAM in the reduction of turbidity and require higher dose of PAC coagulant to produce comparable result of coagulant activity. PAC-MO combination was observed to be comparable to the result obtained with PAC-PAM, reducing the initial turbidity up to 90 %, also it was noted that PAC-MO resulted to a 50 % decrease in the trihalomethanes formation potential rate while PAC-PAM combination increases the potential of trihalomethane formation in water to a level below the permissible limit [44, 45]. An investigation on the use of MO and $Al_2(SO_4)_3$ in the treatment of water reveals that, MO proved more efficient than aluminum sulfate by having high turbidity removal efficiency of 94.9 and 92.5 % for turbidity and color respectively at an optimum dosage of 20 mg/L [46]. The modification of soil/sand with MO extracts has been reported to prove effective in the removal of cyanobacterial blooms, the alga removal efficiency increased with an increase in the initial algae population. Higher ionic strength favored the Microcystis aeruginosa cell removal, while variation in pH (4.34 to 10.04) and organic load concentration (4-40 mg/L) had no significant effect on the alga removal efficiency [47].

Tannin. The use of tannin in water treatment does not affect the alkalinity of the solution because tannin does not contain metals in its structure and therefore does not

undergo hydrolysis. The advantage of using tannin derived coagulant is that its irregular shape provides a great surface area of contact, thereby enhancing efficient flocculation; also, tannin does not alter the pH of the suspension [41, 48, 49]. The use of tannin at dosages of 3.0 and 4.0 mg/L has proved effective in removing up to 91 and 57.3 % of turbidity and total dissolve solids respectively, a pH drop from 7.8 to 6.5 was recorded after the wastewater was treated with the tannin coagulant [48, 49]. For the removal of metal ions and color from wastewater at lower primary coagulant dose, the synergetic use of tannin-aluminum sulfate combination shows significant coagulation efficiency and sludge filterability than the use of aluminum sulfate alone, and the residual aluminum and tannin were greatly reduced and their values fallen below the detection limits [41].

Cactus. The use of cactus as a coagulation aid with $Al_2(SO_4)_3$ for sewage treatment shows that the removal efficiencies were higher for turbidity and COD removal than of cactus or aluminum sulfate alone, it has been noted that the use of opuntia species of cactus in the treatment of turbid water using kaolin clay particles at pH 10, a 98 % turbidity removal was observed for a ranged of initial turbidities. A removal efficiency greater than 90 % for removing suspended solids and COD has been noted when using lime enhance cactus coagulant in the treatment of wastewater, this effectiveness is similar to the use of polyacrylamide and the reason for the similarity in effectiveness has been related to the presence of the same functional group in cactus and polyacrylamide [36, 41].

Plantago species. The use of psyllium husk (PSH) as a primary coagulant is ineffective due to its low surface charge. However, the use of PSH as a coagulant aid for poly aluminum chloride show an increased in the removal performance efficiency of 64, 90 and 97 % for COD, color and total suspended solids compared to the values of 55, 80 and 95 % for COD, color and total suspended solids which was obtained when poly aluminum chloride was used unaided. Similarly, the use of PSH as a coagulant aid for aluminum sulfate shows an increase in the removal performance efficiency of 63, 83 and 81 % for COD, color and total suspended solids compared to the values of 58, 79 and 78 % for COD, color and total suspended solids which was obtained when aluminum sulfate was unaided. PSH is therefore a good coagulant aid for poly aluminum chloride and aluminum sulfate for the treatment of wastewater [41].

Hibiscus rosa-sinensis leaf extract. This plant extract has been used as a coagulant aid with $Al_2(SO_4)_3$ (primary coagulant) in the removal of iron, suspended solids, ammonia nitrogen and turbidity. Research shows that a 60 % removal efficiency of iron was observed when aluminum sulfate was used unaided, while 100 % removal efficiency was observed when aluminum sulfate was used with the plant extract as a coagulation aid. A combination of $Al_2(SO_4)_3$ and the plant extract as a coagulation aid produce 72 % removal for suspended solids compared to the 40 % removal obtained when aluminum sulfate was used unaided. It is therefore suggested that Hibiscus extracts can function effectively as a coagulation aid in the treatment of wastewater [41].

2.1.3. Organic-inorganic coagulant (Alcat and Fercat). This comprises of inorganic coagulant which has been appropriately modified by organic polyelectrolytes examples include Alcat and Fercat. The chemical composition for Alcat comprises poly aluminum chloride along with Al₂O₃ in the amount of 16.10-17.90%, Al³⁺ ions in the amount of 8.5-9.5% and organic polyelectrolyte modifier amounting to 10 %, on the other hand for Fercat, it comprises of iron (III) sulfate along with total iron in the amount of 11.60 to 12.00 %, Fe^{2+} ions in the amount of 0.1 to 0.7 %, and modifiers amounting to 10 % [38]. It was observed that an increase in the dose of Fercat resulted to increasing the percentage removal of both COD and color, while an increase in the dose of Alcat resulted to increasing percentage removal of color. For Fercat, the value of COD reduces from a range of 51 % at a dose of 0.5 mg/L to 66 % at 2.5 mg/L and percentage removal of color ranged from 38 to 88 %. On the other hand, for Alcat the value of COD reduction increases from a range of 60 to 80%, while the color reduction increases from a range of 71 to 93 %. It was therefore noted that the percentage removal efficiency of Alcat was higher than that of Fercat [38].

2.1.4. Electro coagulation. It has been revealed that the removal efficiency for dye, color and heavy metals such as chromium with iron electrode is higher than that of aluminum electrode and the use of hybrid Fe/Al electrode is capable of reducing 99 % of heavy metals such as arsenic [50-52]. Contrary to a research outcome on the combination of electrocoagulation and electrooxidation which reveals that electrocoagulation is only able to reduce half of the COD in wastewater. The combination of electrocoagulation and electro-oxidation has been proposed to exhibit 60 % removal of the initial concentration of COD in wastewater. Furthermore, it has been revealed that the hybridization of electrocoagulation by combining with other techniques (such as electro-oxidation, photolysis degradation, advanced oxidation, adsorption membrane, aerobic and anaerobic process) can result to a removal efficiency greater than 90 % for COD, heavy metals, BOD, color, turbidity, total suspended solids [53, 54].

Research outcome has shown that pH, electrical current, electrical potential, electrode materials and electrolysis time affect the performance efficiency of electrocoagulation. At a pH of 10.2, potential difference of 20 volt and an electrolysis time of 60 minutes, aluminum electrode were observed to have 95.6 % removal efficiency for water hardness [55]. A comparative study on the use of iron and aluminumbased products for the removal of COD and phosphorus form chemically and electrochemically coagulated wastewater revealed that the quantity of phosphorus compounds or compounds responsible for COD, neutralized or adsorbed on colloidal micelles of aluminum or iron hydroxides depends on the applied coagulants or electro-coagulants [56]. It has been observed that aluminum ions from both poly aluminum chloride and aluminum electrodes were equally effective in adsorbing phosphorus compounds while the wastewater coagulated with ferric sulfate has maximum

adsorption with values approximately five times higher than that of the iron electrode. It was also observed that 1 g of aluminum ion from poly aluminum chloride was able to adsorb 47.2 g of the compounds responsible for COD, while iron electro-coagulant was 23 times less effective when compared to poly aluminum chloride for the removal of COD [56]. The aluminum electrode was observed to have a higher maximum adsorption over the iron electrode for the removal of both COD and phosphorus form wastewater. Based on this outcome, it was proposed that poly aluminum chloride is the most effective. While iron electro-coagulant is the least effective for the removal of phosphorus and COD from wastewater and the difference in effectiveness of the aluminum and iron-based product was attributed to influence of anions such the chloride ions from the poly aluminum chloride and the sulfate ions from the ferric sulfate. In addition, it has been shown that chloride ion has a high level of conductivity, flocculation, and dissolution of metal anodes. And an increase in chloride ion concentration will lead to an increase the removal percentage of turbidity, color, phosphate, suspended solids and other pollutants [54, 56-58]. The performance of iron electrodes has been compared to that of ferric sulfate in electrocoagulation and chemical coagulation respectively. It was observed that at a current intensity of 0.4 A and an electrolysis time of 40 minutes, the removal efficiency after electrocoagulation was 71.15, 98.26 and 86.59 % for COD, color and turbidity respectively, while the chemical coagulation has a removal efficiency of 83.17, 99.81 and 98.62 % respectively for COD, color and turbidity respectively [58]. Despite the higher removal efficiency of ferric sulfate over iron electrode, electrocoagulation result in near neutral pH values and a decrease in conductivity, by contrast chemical coagulation alters the pH of the system and increases the acidity and conductivity of the effluents [54]. Moreover, it has been noted that despite the wide applicability of both chemical and electrocoagulation due to their high removal efficiencies for color, COD, BOD, heavy metals, total suspended solids, turbidity, organic matter, pathogens, nutrients such as nitrate and phosphorus. Chemical and electrocoagulation methods exhibit some shortcomings such as relative high procurement cost for developing countries, vulnerability to temperature variation, technical skills and training, alteration of the pH of the treated water, the production of large volume of sludge and detrimental effect on human health. Aluminum based coagulants has been strongly linked to the development Alzheimer's disease in humans. The demerits of chemical and electrocoagulation have necessitated the development of cost effective and ecofriendly green bio-based coagulants in order to counteract the aforementioned demerits [29, 39, 40, 54, 55, 58-60].

2.2. Biological treatment

Biological method of treating wastewater is also an effective treatment method that has been widely accepted by the scientific community. This treatment method can be classified into aerobic treatment and anaerobic digestion treatment process.

2.2.1. Aerobic treatment method. Aerobic treatment is a biological process whereby microorganisms breaks down organic matter by utilizing oxygen, this method of treatment is directly used after the physical/chemical treatment method or after the anaerobic treatment method. This is because anaerobic treatment method is not effective enough when used in the reduction of organic matter to an acceptable level of discharge into the environment. Aerobic treatment has the advantages of low odor production, no required optimum temperature, low cost of operation and fast biological growth rate. The availability of dissolved oxygen is essential for the microorganisms involved in aerobic treatment process in order to reduce the organic matter present in the wastewater [20]. Research in the removal of nitrogen from wastewater by using microalgae and microalgae-bacteria has been successfully reported. It has been observed that microalgae and bacteria are sensitive to their environmental factors such as light supply, lighting period, pH of algae and microalgaebacteria growth media, microalgae and bacterial species, dissolved oxygen in aquatic media and organic matter, which affect the activity and performance of the microalgae system for aerobic treatment method [61].

2.2.2. Anaerobic digestion treatment method. Anaerobic digestion method is a biological process which results to the breaking down of organic matter by microorganisms in the absence of oxygen. This method of biological treatment is less effective than the aerobic treatment method for the reduction of organic matter present in wastewater but has the advantage of low cost of operation when compared to aerobic treatment method. Anaerobic digestion process produces biogas (a blend of methane and carbon (iv) oxide) and digestate (solid byproduct), the success of this biological treatment method is highly dependent of the primary physico-chemical treatment step [62].

3. Comparison between the efficiency of chemical and biological treatment techniques

It has been reported that chemical coagulation is more effective than electrocoagulation in removing total organic carbon, while electrocoagulation is more effective than chemical coagulation at removing iron. also been However. it has reported that electrocoagulation has a high removal efficiency of color, chemical oxygen demand, and biological oxygen demand. Also, electrocoagulation produces lesser volume of sludge and requires lesser time than chemical coagulation to achieve an optimum result in removing pollutants from wastewater [54]. Comparative study has shown that the reduction removal of COD and total suspended solids were 83 and 90 %, 78 and 93 %, 84 and 97% by biological treatment, chemical and electro coagulation respectively. These methods have a relatively close range in their percentage performance but the difference between the three methods is the time required to achieve the above results. The results obtained by biological treatment require two and half hours, chemical coagulation requires 45 minutes while electrocoagulation requires 30 minutes. The biological method requires more time than the chemical and

electrocoagulation methods. However, the biological method produces lesser volume of sludge than the coagulation methods. Unlike the biological treatment which requires specific conditions, such as light supply, lighting period, pH, microorganisms' growth media and species, dissolved oxygen and nutrient, therefore limiting the ability to treat large volume of wastewaters with high toxicity. Electrocoagulation can be used to treat multifaceted wastewaters, including industrial, agricultural, and domestic effluent [54, 60-64].

4. Conclusion

Chemical treatment method that involves the use of inorganic coagulant such as aluminum sulfate has low performance efficiency in cold water and aluminumbased coagulant has been strongly linked to the development of Alzheimer disease in humans. Synthetic organic compound which can either be used as a primary coagulant or coagulant aid has the problems of nonbiodegradability and toxicity. This has resulted to a quest in their substitution by using natural organic based coagulant. Biological method has also been noted to be effective in the treatment of wastewater but require more time than chemical method for a desirable result and the level of performance in removing pollutants from wastewater depends on certain crucial environmental factors.

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Conflict of interest

Authors declare no conflict of interest.

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