Evaluation of Inorganic Coagulants in the Removal of Turbidity, Electrical Conductivity and Chemical Oxygen Demand in Wastewater

Ukiwe L. N., Ibeneme S. I., Alisa C. O., Chijioke-Okere M.

1Department of Chemistry, Federal University of Technology, Owerri, Nigeria
2Department of Geosciences, Federal University of Technology, Owerri, Nigeria

Email address
luggil2002@yahoo.com (Ukiwe L. N.), peseesabim@yahoo.com (Ibeneme S. I.), alisaallosa@yahoo.com (Alisa C. O.), oby.chijioke85@gmail.com (Chijioke-Okere M.)

Citation

Abstract
The ability of four inorganic coagulants namely; aluminum sulphate octadecahydrate ($\text{Al}_2\text{(SO}_4\text{)}_2\cdot18\text{H}_2\text{O}$), ammonium aluminum sulphate dodecahydrate ($\text{NH}_4\text{Al(SO}_4\text{)}_2\cdot12\text{H}_2\text{O}$), ammonium ferrous sulphate ($\text{(NH}_4\text{)}_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}$) and ferrous sulphate ($\text{FeSO}_4$) was investigated to alter the amounts of turbidity, electrical conductivity, and chemical oxygen demand (COD) in wastewater. Results obtained from experiments indicated that maximum turbidity removal was achieved using FeSO$_4$ (98.5) at 180 mins, while ($\text{(NH}_4\text{)}_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}$) presented the overall least removal rate. The best COD removal (90%) was also achieved at 150 mins using ($\text{(NH}_4\text{)}_2\text{Fe(SO}_4\text{)}_2\cdot6\text{H}_2\text{O}$). It was observed that application of the coagulants didn’t completely eliminate COD from the wastewater, while the electrical conductivity was slightly affected by the four coagulants.

1. Introduction
Coagulation is a process which is used to remove the turbid materials in water and wastewaters. In water treatment, when the feed water has been screened and passed through optional steps of pre-chlorination and aeration, it is then treated through the coagulation-flocculation process. All types of waters, especially surface water contains both dissolved and suspended particles. Coagulation and flocculation are processes which are employed to remove the dissolved and suspended particles. The suspended particles vary considerably in source (origin of the suspended particles), composition charge, particle size, shape and density. The success of the coagulation and flocculation processes depends on the understanding of the interactions between the factors that affect both suspended particles and water molecules. The surface charge of the particles plays a significant role in stabilizing the particles. Most of the particles in water and wastewater have a negative charge and thus repel one another when they come in contact.

Coagulation/flocculation occurs in successive steps and the process uses coagulants that destabilize suspended particles forces, hence, allowing the particles to come together, collide and form settleable particles in the form of flocs [1]. The primary purpose of the coagulation/flocculation process is to remove turbidity caused by...
dissolved and suspended particles in water. In addition, the process also removes many bacteria, and the chemical oxygen demand (COD); also, electrical conductivity of the wastewater can change during the reactions.

During the process of coagulation/flocculation, coagulants are added to the wastewater to overcome the repulsive forces and increase the van der Waals forces of attraction in the system. Colloidal particles collide and form flocs, and further collision occurs resulting in the formation of larger flocs. Coagulants have the following classification: inorganic coagulants (aluminum sulphate (Al₂(SO₄)₃ or alum), ferric chloride (FeCl₃), ferrous sulphate (Fe₂SO₄)[2].

- organic coagulants (polymers and synthetic polyelectrolytes with anionic or cationic functional groups such as polydiallyldimethyl ammonium chloride)[3].
- natural coagulants (Paparin, Moringa oleifera)[4].
- electrochemical coagulants (electrochemical cells)[5].

Coagulants selection should be based on the following principles:
- good coagulation effect.
- non toxicity.
- low cost.
- must meet health authority standards.
- adaptability to function at a wide range of pH.

The studies on the use of coagulants have shown that iron salts such as FeCl₃ and FeCl₂ have the ability to significantly affect turbidity, pH and COD of solutions of humic acids [6]. Further studies have revealed that treating textile wastewater with lime alone proved to be very effective in removing color and COD from wastewater. However, a combination of FeSO₄ with lime, and regulating the pH in the range of 9.0 was observed to be more effective in the elimination of color and COD in wastewater [7]. In a related study, Kim and Kang [8] observed that iron (III) nitrate (Fe(NO₃)₃) was also able to reduce turbidity in kaolin dispersed solutions. The study noted that effective flocculation was achieved by the precipitates of ferric hydroxide (Fe(OH)₃) formed at elevated pH (9.0). However, as the coagulant dose is increased, interparticle collision and aggregation is enhanced.

Comparing the ability of lime, alum, and FeCl₃ in removing COD and surfactant in wastewater, Amir et al. [9] observed that FeCl₃ was the most effective coagulant, removing almost 80 and 89% of surfactant and COD. Attempts have also been conducted to model the relationship between raw water quality parameters such as turbidity, pH buffering capacity and dosages of the coagulants such FeCl₃ and alum for the removal of organics in wastewater [10]. Alum has been documented as a widely used coagulant in wastewater treatment [11,12]. Recently, a review by Aziz et al. (2004) noted that alum and FeSO₄ could be applied in combination to successfully reduce COD in wastewater. Ukiwe et al. [13] had also documented evidence suggesting that when aluminum chloride (AlCl₃), FeCl₃ and alum were jointly used in the coagulation/flocculation process; there was an enhanced turbidity removal in wastewater. It has been reported that the optimum pH and dosage for alum to effectively remove COD in waste streams exhibit values between 6.5-10 and 1-1.4 mg/L, respectively [14].

Polymers have successfully been employed in the water/wastewater treatment, and have shown the following advantages over inorganic coagulants: require lower coagulant dosage, the sludge volume formed during coagulation is small, operates at a wide range of pH (5.0-10.0), and could be applied at low water temperature. Polyacrylamides can also remove COD in wastewater [15]. When anionic and cationic polyacrylamides were applied to remove turbidity and COD in slaughterhouse wastewater, it was observed that the addition of FeCl₃ or polyaluminum chloride to anionic polyacrylamide led to significant reduction of turbidity and COD [16]. Nonetheless, in a separate study, Liang and Wang [17] stated that the addition of polyferric sulphate to cationic polyacrylamide did not effectively remove turbidity and COD in wastewater. However, further studies on the use of polymers in wastewaters treatment have been reported by Bae et al. [18], Park and Yoon [19], and Ajzawa et al. [20], who separately investigated the use of polyacrylamide based flocculants, diatomite as well as synthetic polyelectrolytes coagulants in wastewater treatment.

Electrochemical methods such as electrocoagulation and electrooxidation have been extensively applied in coagulation/flocculation process for treating wastewaters recently [21, 22, 23, 24].

Recent advances have noted that extracts from microorganisms, animal or plant tissues can also act as natural coagulants in the reducing turbidity and COD from wastewater [25]. In order for natural coagulants to be effective in the coagulation/flocculation process they should be cost effective, biodegradable, safe for human health, and produce less sludge. Moringa oleifera is comparable to inorganic chemicals and polymers in terms of treatment efficiency when the plant is applied to treat wastewater [26].

The measurements of turbidity, electrical conductivity and COD are the key indicators of the quality of water and wastewaters. Significant changes in turbidity and electrical conductivity values showed that the pollution of water or waste streams systems is inevitable.

The aim of the present study was to evaluate the effectiveness of Al₂(SO₄)₃.18H₂O, NH₄Al(SO₄)₂.12H₂O, (NH₄)₂Fe(SO₄)₂.6H₂O and Fe₂SO₄ in removing turbidity, electrical conductivity and COD from wastewater.

2. Materials and Method

The laboratory reagents and chemicals used in this research were all analytical grade obtained from BDH Chemicals, UK. The following instruments were also used. pH meter (model PHS 25, Shanghai Automation Instrumentation Co., China), turbidimeter (model WGZ-1B, Shangai Xinrui Instruments, China), electrical conductivity meter (model DDS-11A, Shjinmai Instruments, China), COD...
The wastewater used in this research was obtained from the Otamiri pond, in Owerri, Nigeria. It is important to point out the importance of treating this water, what are the main characteristics to improve in order to use this water. Three 5 L plastic containers previously washed and rinsed with distilled water were used to collect the sample. Three samples were separately collected at a distance of 500 meters each. The three samples were then mixed together to form a homogenous mixture in a 20 L plastic container, previously washed and rinsed with distilled water. The mixture (sample) in the 20 L plastic container was then transferred to the Project Laboratory of the Department of Chemistry, Federal University of Technology, Owerri, Nigeria. The debris in the sample was allowed 2 h settling after which the suspended solid particles were decanted. The resultant mixture was then used as the stock sample for analysis.

2.2. COD Experiment

About 5 mL of the remaining 10 mL of the mixture allocated for COD determination was withdrawn using a syringe and poured into 100 mL conical flask. About 3 mL of potassium dichromate reagent and 7 mL sulphuric acid reagent were measured, respectively, and poured into the conical flask. The top of the flask was capped using a rubber cork. The mixture was stirred for 3 mins, and placed inside a COD digester at 110°C for 30 min and thereafter, the conical flask was withdrawn from the digester and the digestate cooled in a water bath to room temperature. Approximately, three drops of ferroin indicator were added to the digestate in the conical flask and stirred for 3 mins. The resultant mixture was titrated with 0.1 M ferrous ammonium sulphate (FAS) solution to a reddish brown color. The COD of the sample was obtained using the formula:

$$\text{COD} = (X - Y) \times M \times 8000/\text{mL of sample used} \quad (1)$$

Where $X = \text{mL of FAS solution for the control experiment}$

$Y = \text{mL of FAS solution for the sample}$

$M = \text{molarity of FAS}$

$8000 = \text{milliequivalent weight of oxygen x 1000 mL/L}$

Three repeats were performed and the mean COD (mg/L) value was obtained. This procedure was repeated at 60, 90, 120, 150, 180 and 210 min., respectively. However, the entire procedure was also repeated using NH₄Al(SO₄)₂.12H₂O, (NH₄)₂Fe(SO₄)₂.6H₂O and FeSO₄ salts.

The above procedures for determination of turbidity, electrical conductivity, and COD were conducted with the stock solution without adding any of the coagulants. This experiment was conducted as control experiment to know the turbidity, electrical conductivity, and COD of the raw wastewater sample.

### 3. Results and Discussion

#### Table 1. Values of turbidity, electrical conductivity and COD of the raw wastewater sample.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Mean values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>20</td>
</tr>
<tr>
<td>Electrical conductivity (µs/cm)</td>
<td>10.05</td>
</tr>
<tr>
<td>COD (mg/L)</td>
<td>160</td>
</tr>
</tbody>
</table>

#### Table 2. Values of turbidity of the four inorganic coagulants at various times.

<table>
<thead>
<tr>
<th>Coagulants</th>
<th>Alum (%)</th>
<th>(NH₄)₂Fe(SO₄)₂.6H₂O (%)</th>
<th>(NH₄)₂Al(SO₄)₂.12H₂O (%)</th>
<th>FeSO₄ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>66</td>
<td>5</td>
<td>86</td>
<td>86</td>
</tr>
<tr>
<td>60</td>
<td>64</td>
<td>15</td>
<td>87</td>
<td>88.7</td>
</tr>
<tr>
<td>90</td>
<td>78</td>
<td>18.3</td>
<td>89</td>
<td>94.9</td>
</tr>
<tr>
<td>120</td>
<td>87</td>
<td>19.4</td>
<td>90.8</td>
<td>95.3</td>
</tr>
<tr>
<td>150</td>
<td>91</td>
<td>26.2</td>
<td>92.2</td>
<td>95.4</td>
</tr>
<tr>
<td>180</td>
<td>91</td>
<td>28.1</td>
<td>92.4</td>
<td>98.5</td>
</tr>
<tr>
<td>210</td>
<td>92.3</td>
<td>31</td>
<td>92.7</td>
<td>97</td>
</tr>
</tbody>
</table>
The turbidity values (%), electrical conductivity and COD versus time using the four inorganic coagulants for coagulation are shown in Table 2-4. A decreasing trend was observed with turbidity when the time increased from 30 to 210 mins. FeSO$_4$ yielded the best turbidity removal efficiency (98.5%) after 180 min., while (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O showed to be the least effective salt in the removal of turbidity in the wastewater. The present study observed a slight alteration of water electrical conductivity by the four coagulants. Regarding the turbidity removal, the findings of the present study agreed with data published by Domopoulou et al. [27], who reported that iron salts were effective in reducing turbidity in the wastewater, though the researchers noted that iron (III) salts were more effective than iron (II) salts.

The highest COD removal efficiency (90%) in the present study was achieved using (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O at 150 mins. However, the COD values obtained for alum, NH$_4$Al(SO$_4$)$_2$.12H$_2$O and FeSO$_4$ after 150 mins were 40, 80, and 20%, respectively. These values indicate that FeSO$_4$ was not an effective coagulant in removing COD in the wastewater. It was also observed that the application of the four coagulants separately, didn’t completely remove the COD in the wastewater. Libecki and Dziejowski (2010) had earlier reported that redox reactions between iron (II) and iron (III) ions in the presence of dissolved organic substances inhibit the ability of iron salts to initiate photooxidation of organic substances in the wastewater. These findings support the observation in the present study with regard to the performance FeSO$_4$ in coagulation.

Solmaz et al. [28] had observed a 62 and 64% removal efficiency of COD in biologically pre-treated textile wastewater using iron (II) and (III) salts. The authors, however, demonstrated that the high performance of both iron salts was due to the high dosage of salt (400mg/L) as well as the biological pre-treatment of the wastewater. Pre-treating wastewater biologically reduce the COD content of a wastewater. The findings of the present study have revealed that high removal efficiency of COD could still be achieved without pretreatment of the wastewater. However, the present study would encourage more studies on the use of iron salts to completely remove COD and turbidity from wastewaters in order to fully understand and explain the action of the salts in coagulation/flocculation process.

### 4. Conclusion

The present study examined the effect of four inorganic coagulants (Al$_2$(SO$_4$)$_3$.18H$_2$O, NH$_4$Al(SO$_4$)$_2$.12H$_2$O, (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O and FeSO$_4$) on the removal efficiency of turbidity, electrical conductivity, and COD in wastewater. ‘jar test’ experiments conducted revealed that the highest turbidity removal efficiency was achieved by FeSO$_4$ (98.5%) at 180 mins, while the highest COD removal efficiency (90%) was also achieved at 150 mins using (NH$_4$)$_2$Fe(SO$_4$)$_2$.6H$_2$O. It was however observed that the four inorganic coagulants didn’t have a noticeable effect on the electrical conductivity of the wastewater. The findings of the present research have clearly shown that FeSO$_4$ in approximately 3 h was effective in totally eliminating colloidal particles from wastewaters.

### References


