



Purification of petroleum produced water by novel *Afzelia africana* extract via single angle nephelometry



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ABSTRACT

Treatment of petroleum produced water (PPW) using jar test and novel *Afzelia africana* coagulant (AAC) has been investigated. AAC was a by-product of sequential ethanol–multiple salts oil extraction from the precursor seed. Process kinetics, statistical analyses and removal efficiency at varying PPW pH and AAC dosage were evaluated. Optimum treatment conditions were obtained at dosage of 100 mg/L, pH of 4, period of 59.5 s and rate constant of $2E-05 \text{ m}^3/\text{kg}\cdot\text{s}$. Comparatively, at optimum, AAC and alum recorded 81.28% and 79.10% removal efficiencies, respectively. It could be concluded that AAC was relatively more effective for the treatment of PPW at the conditions of the experiment.

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Introduction

Nigeria's economy is based on petroleum exploitation. This has contributed immensely to the degraded aquifers in the Niger delta region due to incessant oil spills and discharges of ill-treated PPW on both terrestrial and aquatic environments. Produced water is a complex mixture of dissolved and particulate organic and inorganic chemicals in water. These chemicals usually comprise of water-soluble, low molecular weight organic acids, monocyclic aromatic hydrocarbons such as alkyl phenol, and metals such as barium, iron, manganese, mercury, zinc etc. [1]. The discharge of untreated PPW results in loss of farmlands, low crops yield, impaired aquatic life, low water quality and prevalence of water-borne diseases [2]. Thus, it is very important to treat the PPW to maintain environmental integrity.

Waste water treatment methods abound, and they include: alkaline chemical precipitation by lime addition, adsorption, ion exchange, reverse osmosis, oxidation, neutralization, membrane filtration, coagulation and flocculation etc. [2]. Of these methods, coagulation–flocculation clearly presents feasible initial core treatment option for primary purification of PPW [2–4]. The major advantages of coagulation–flocculation process over other methods of waste water treatment include: (1) excellent

performance in turbidity, inorganics, pathogens and natural organic material removal (2), cost effectiveness (3), easy to operate and relatively less energy consumption [5–7].

Coagulation–flocculation is the tendency of the particulates phase of colloidal dispersion to aggregate into flocs of large conglomeration of elementary particles within the occluded liquid [8]. Wang et al. [9] demonstrated that the efficiency and rate of coagulation depends on pH, effluent turbidity, and nature of coagulant, temperature and mixing effect.

Conventionally, inorganic coagulants such as aluminum sulfate (alum), calcium hydroxide and ferric chloride have been widely used to remove a broad range of impurities from effluents. However, these salts have inherent draw-backs that include: impact on the pH of water, increase in the volume and metals content of sludge, resulting in high disposal cost. Furthermore, residual aluminum concentration in treated water has raised public health concerns [10]. It has been reported that extensive intake of alum could cause Alzheimer's diseases [11].

Consequently, the search for better alternatives to conventional coagulants has become an important challenge, providing platform for the consideration of eco/health friendly coagulants of biological origin. Biologically originated coagulants are usually presumed safe for human and environmental health, since they are extracts from edible plants and animals. Among these biocoagulants/ flocculants are chitosan, tannins, *Moringa oleifera* [12] and *Afzelia africana* seed, which is the subject of this study.

Afzelia africana seed, which is native to the tropical climate such as Nigeria, is of leguminous plant, relatively rich in edible

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carbohydrate, fat and protein [13]. The seeds are cheaply abundant in Eastern Nigeria and had been successfully subjected to novel trials for the treatment of brewery and coal effluents. Successes achieved in the previous applications of AAC, provided the impetus to extend its use in the purification of PPW, which is currently posing an environmental challenge in the Nigeria's Niger Delta region [1].

In this work, the response monitored at varying pH and dosage was the residual turbidity, which was used for the evaluation of kinetics and efficiency of the process by application of statistical tools like analysis of variance (ANOVA) and Tukey test. In its simplest form, ANOVA provides a statistical test of whether or not the means of several groups are equal, and therefore generalizes *t*-test to more than two groups. Doing multiple two-sample *t*-tests would result in an increased chance of committing a type I error [14]. For this reason, ANOVAs are useful in comparing (testing) three or more means (groups or variables) for statistical significance.

When differences between groups exist, a post hoc test can be applied to identify how the groups differ among themselves. Post hoc tests are methods for pin-pointing the sources of particular significant differences among group means. Applied here is Tukey's HSD (honest significant differences) test, which is a post hoc test that determines whether three or more means differ significantly in an ANOVA.

This work therefore, elicits interest in the utilization of AAC for the purification of PPW, while also, demonstrating statistical implications of the pH and dosage variations during the purification process. Furthermore, the effects of pH and dosage variations on the kinetics and efficiency of the coagulation–flocculation were investigated.

Materials and methods

Materials collection and preparation.

Petroleum produced water (PPW)

PPW sample was collected from a major petroleum refinery complex in Warri, Nigeria and stored in black plastic container to prevent photo catalyzed changes in the characteristics of the PPW.

Afzelia africana seed sample

Afzelia africana samples (precursor to AAC) were picked from Nsugbe, Anambra State, Nigeria. 2 kg of dry sample was de-hulled to remove the red cap and subsequently milled to obtain a ground dried sample of 0.6 mm.

AAC was prepared as a by-product of oil extraction according to a modified method of Sutherland [15]. In this method, 30 g of sieved *Afzelia africana* seed powder was firstly soaked in ethanol and the mixture continuously stirred by magnetic stirrer for 1 h, after which it was filtered using whatman filter paper no 3. The resulting residue was poured into a beaker containing 1:25 w/v mixture of chloride salts solutions (0.7 g/L CaCl₂, 4 g/L MgCl₂, 0.75 g/L KCl, 30 g/L NaCl), which was stirred by magnetic stirrer for 1 h, (to provide resident time that allows for adequate mixing, inter-facial contacts and mass transfer) and subsequently filtered using Whatman no. 3 filter paper to remove spent solid. The filtrate was poured in a sufficiently agitated beaker, and firstly heated to a steady temperature of 70 °C. The heating at 70 °C was maintained for 1 min to set up precipitation of desired coagulant out of the filtrate solution. The remaining liquid filtrate was separated from the precipitate, which was allowed to dry into solid mass of coagulant (AAC) under ambient condition.

Materials characterization

Petroleum produced water

Sample characterization was done in accordance with the standard methods for the examination of water and wastewater [16]. Table 1 presents the characteristics of PPW.

Table 1

Characterization result of PPW.

Parameter	Value	Unit
pH	7.6	
Fe ²⁺	0.711	mg/L
SO ₄ ^{2−}	26	mg/L
NO ₃ ^{2−}	12.8	mg/L
Alkalinity	44	mg/L
Acidity	172	mg/L
Ca ²⁺	Nil	mg/L
Mg ²⁺	Nil	mg/L
Salinity	5618.66	mg/L
Turbidity	715	NTU
Conductivity	12.17	ms/mc
Total dissolved solids	5901.12	mg/L
Total suspended solids	943.5	mg/L
COD	10	mg/L
Hydrocarbon	99.7	mg/L

Afzelia africana sample

The physical and chemical characteristics of *Afzelia africana* seed flour were determined as described in Sections "Determination of percentage yield and weight loss" to "Determination of percentage protein". The results are shown in Table 2 and Fig. 1.

Determination of percentage yield and weight loss. 30 g of *Afzelia africana* seed flour was processed as described in Section "Afzelia africana seed sample" into W (g) AAC. The percentage yield and percentage weight loss were calculated using Eqs. (1) and (2):

$$\text{Percentage yield} = \frac{W}{30} \times 100 \quad (1)$$

$$\text{Percentage weight loss} = \frac{30 - W}{30} \times 100 \quad (2)$$

Determination of bulk density. 100 mL container was tap-filled (to 100 mL mark) with 50.78 g seed flour to obtain bulk density using Eq. (3).

$$\text{Bulk density} = \frac{W}{V} \quad (3)$$

where W (g) is weight of the sample powder and V (mL) is volume of the container.

Percentage ash content determination. 2.0 g of the seed powder was put in crucible and burnt over a Bunsen burner flame until no smoke was evolved. The sample was heated in the muffle furnace at 600 °C until seed powder turned gray–white. On cooling, ash content was determined using Eq. (4).

$$\text{Ash content}(\%) = \frac{W_{\text{ash}}}{W_{\text{sample}}} \times 100 \quad (4)$$

Table 2

Proximate analysis of *Afzelia africana* seed powder.

Parameter	Value
Yield (%)	91.39
Weight loss (%)	8.61
Bulk density (g/mL)	0.5078
Ash content (%)	8.7
Oil content (%)	8.6
Moisture content (%)	33.5
Protein content (%)	32.3

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