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Focus on adsorptive equilibrium, kinetics and thermodynamic components of petroleum produced water biocoagulation using novel *Tympanotonos Fuscatus* extract

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ABSTRACT

Adsorptive component of produced water (PW) coagulation using *Tympanotonos Fuscatus* coagulant (TFC) was studied. Influence of the following parameters: pH, coagulant dose, settling time, and temperature were investigated. The functional group, crystalline nature, morphological observation and thermal characteristics of the sample were evaluated. Equilibrium data were analyzed using Langmuir, Freundlich, Temkin, Frumkin, and Dubinin-Radushkevich (D-R) adsorption isotherms. The kinetics data were fitted to reversible first order, pseudo-first-order, pseudo-second-order, elovich, intra-particle diffusion and Boyd kinetic models. Adsorption Gibbs energy, enthalpy and entropy were evaluated. Equilibrium data best fitted the Langmuir isotherm ($R^2 > 0.99$; $X^2 < 1.6$; SSE < 1.6). Reversible first order model correlated best to the kinetics data. The values of process average Gibb's free energy, enthalpy and entropy were 30.35, 27.88 and 0.1891 kJ/mol, respectively. The process was spontaneous, feasible and endothermic in nature. The maximum efficiency of 83.1% was favored at pH 2.0. This study indicated significant adsorptive component, while using *Tympanotonos Fuscatus* extract as readily available, renewable, ecofriendly bio − coagulant for efficient treatments of PW.

1. Introduction

Water is a fundamental need of man. In Nigeria, due to the negligence of regulatory standards, availability of healthy water presents a huge challenge [1]. Nigeria's economy is petroleum based. In the Niger delta region, continual oil spillage and discharge of poorly treated PW on both terrestrial and aquatic environments have impacted negatively on the surface and underground water resources [2]. Produced water is an effluent that is present in the underground hydrocarbon reservoir and is discharged to the surface along with the crude oil or natural gas.

Components of produced water include suspension particles, dissolved particles, oil droplets, salts etc [3]. Enriched PW in the environment constitute a severe health hazard to both plants and animals and would threaten the functionality of the ecosystem.

Therefore, there is increasing need to ensure PW meets regulatory standard [4] before being discharged to the environment. PW can be treated in many different ways, such as dissolved air precipitation, chemical/electrochemical oxidation, biological degradation, and coagulation/flocculation [5–9]. Among these treatment options, coagulation/flocculation presents feasible initial core treatment process for the removal of organic and inorganic particles [1].

Coagulation is a process where particles are destabilized by a coagulant to promote aggregation. Flocculation results in the further build-up of the aggregate into settleable flocs under gravity [10]. Traditionally, inorganic and organic substances such as alum, iron, polyamine, calcium hydroxide have been widely used in the treatment of industrial wastewater [11].

However, these traditional coagulants have major disadvantages

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of high sludge volume [11]. Specifically, aluminum salt residual in the treated water has been linked to Alzheimer's disease [9,12].

As a result of these disadvantages, the quest for better alternatives to traditional coagulants becomes crucial. The present study, considered the usage of ecofriendly bio-coagulant. Among these bio-coagulants/flocculants are Snail shell, Nirmali seeds (*Strychnos potatorum*), *Moringa oleifera*, Tannin, *Cactus*, *Muccuna flagelipes* and *T. Fuscatus* shell [13] which is the subject of the study.

In the present work, the TFC application is being extended to treatment of PW, with emphases on the adsorptive component of the process. Bio-coagulation exhibits two principle mechanisms: (a) adsorption and charge neutralization, (b) adsorption and interparticle bridging [14,15]. Generally, adsorption describes the property of a solid or liquid to attract and stick to its surface a gas, liquid, solute or suspension. In this process, the sticking substances do not enter the solid's minute pores as in absorption.

According to the author's knowledge, previous work is concentrated on adsorptive coagulation (for mineral coagulants), with little or no work done until now on the adsorptive component of bio-coagulation process using TFC for the treatment of PW. Therefore, this paper seeks to close this gap and provide insight into the adsorptive components of PW bio-coagulation. Data obtained from this coagulation studies were examined in the light of adsorption kinetics, isotherm and thermodynamics. Instrumental and physiochemical analyses were used to characterize the samples. Impacts of process factors were also investigated.

2. Materials and methods

2.1. Material collection and preparation

2.1.1. Produced water

PW (contained in black rubber jerrycan to arrest photo reaction) was obtained from a gas and oil facility at Port − Harcourt, Rivers State, Nigeria. PW was characterized on arrival to the lab and subsequently stored in a fridge to avoid degradation.

2.1.2. T.Fuscatus shell (*TFS) and TFC*

TFS was obtained from Onitsha local Market, Nigeria. TFS was thoroughly washed and processed to TFC based on the modified procedure reported elsewhere [16]. In this method, deproteinization of ground TFS sample was firstly achieved by stirring continuously 0.5 L of 1 M NaOH solution containing 50 g TFS powder for 2 h at 70 °C. On cooling, the mixture was separated and resulting solid sample was washed with distilled water for 30 min and subsequently dried (at 70 °C for 2 h) using oven. The deproteinized powdered TFS was demineralized for 30 min in a constantly stirred 0.25 L-1M HCl solution, and the resulting TFS-HCl mixture separated using filter paper. The resulting solid mass was washed thoroughly using distilled water for 30 min, and followed by oven drying at 70 °C for 2 h. The ground TFS obtained after demineralization was deacetylated using auto-clave (at 15 psi) for 30 min at 122 °C using 50% concentrated NaOH solution, applied at 1:10 (w/v) solid to solution ratio. The sample produced after auto-claving was washed to pH 7 using running distilled water and subsequently oven dried for 2 h at 70 °C. This processing end product of ground TFS was termed TFC.

2.2. Material characterization

2.2.1. Produced water

Standard APHA methods, as reported by Clesceri et al. [17], were applied to determine the physical characteristics of the effluent (PW).

2.2.2. TFS

The determination of physical and chemical characterization of *T. Fuscatus shell* such as yield/weight loss, bulk density, ash content, oil content, moisture content and protein content were determined based on the procedure reported elsewhere [2].

2.2.3. Instrumental characterization of TFC

Models Thermo Nicolet Nexus 470/670/870 FTIR Spectrophotometer, Philips X PERT X-RAY diffraction with Cu kr radiation (30kv and 30Ma), TGA − Q50 and DSC − Q200; and Zeiss Evo®MA 15 EDX/WDS were used to characterize the relevant samples.

2.3. Coag − flocculation experiment

The procedure for jar test is described in steps below:

2.3.1. Influence of TFC dosage on efficiency

(i) The initial pH and turbidity of PW samples were determined at room temperature.
(ii) 1000 mL of the PW samples were poured into a specified number of 1000 mL beakers and subsequently dosed with 0.5−5 g/L of TFC.
(iii) The mixtures of the PW and TFC contained in the 1000 mL beakers were subjected to rapid mixing at 110 rpm for 2 min, followed by slow mixing at 35 rpm for 20 min. The treated PW was allowed to settle, at the end of slow mixing for 30 min. During the 30 min settling period, 15 mL of the supernatant from upper layer of the settling effluent was respectively pipetted from 2 cm depth into 50 mL plastic bottles and measured for residual turbidity. Particle concentration in (mg/L) was determined as a product of T_f and residual turbidity [18]. $T_f = 2.35$ was a conversion factor.

2.3.2. Influence of PW pH variation

The optimum dosage obtained in subsection 2.3.1 was used in the evaluation of pH influence. The following procedure steps were used.

i. Exact values of optimum dosages of TFC were dosed into specified numbers of beakers, each containing 1000 mL of PW. The PW pH was adjusted to 2−9 at increments of 1 using 0.1 M H_2SO_4 and 0.1 M NaOH just before dosing of the TFC.
ii. Step (iii) described in subsection 2.3.1 were repeated with respect to variation of pH, resulting in optimum pH determination.

2.3.3. Temporal variation of adsorption capacity with dosage

i The procedure steps (i - iii) described in subsection 2.3.1 were repeated.
ii During settling, residual turbidity was measured at 3, 5, 10, 15, 20, 25 and 30 min for each dosage investigated.

2.4. Analytical method

Eqs (1) and (2) were used to calculate the adsorptive capacity q_t (mg/g) and percentage turbidity removal (% Rem), respectively.

$$q_t = \frac{C_{0-C_t}}{m} \times V \quad (1)$$

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