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Mathematical model to monitor the inhibiting effect of pH on the adsorption of crude oil in bioremediation

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ABSTRACT

The appropriate and effective materials used for oil spill clean-up are becoming of great interest to researchers. This is due to the need for an environmentally acceptable process. In this work, theoretical and mathematical tools were applied to investigate the influence of pH as an inhibiting parameter for the suitability of sawdust for oil spill clean-up. One of the functional parameters that could influence the rate of bioadsorption of an absorbent material such as sawdust is the pH. The rate of absorption with respect to pH was developed using developed models for the study, the maximum specific rate and the equilibrium constant were developed. The rate of bioadsorption applying hardwood, semi hardwood and softwood were thoroughly investigated. The study is imperative and useful because it will be applied in predicting and monitoring the rate of Bioadsorption using this material as an absorbent for effective remediation of contaminated aquatic environment.

Keywords: bioremediation, absorbent, sawdust, pH, inhibiting parameter

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INTRODUCTION

When oil is discharged to an environment, it can cause large biological and physiological effects and a wide range of ecological changes [1] . Crude oil exposure can affect the microbial activity in an Environment [2].This work explores the use of natural absorbents and its effectiveness in bioremediation process such as its p^H..It is very necessary to test the suitability and capabilities of this sawdust to enable researchers know its behaviour during clean-up operations. Several studies have been made to investigate the effects of crude oil spills on the ecosystem and the use of available natural materials for oil spill clean-up [3]. Several materials and instruments have been developed for clean-up of oil on water surface. The materials in use include natural and synthetic sorbents [4, 5]. Since different materials used for oil spill clean-up have different performance and effects on the environment under evaluation, use of an absorbent material whose physiochemical properties are known will be of great importance. Oil spills are certain to happen and their prevention are important. Based on these factors, the use of absorbents for oil spills become imperative. Sorbents are materials which recover oil through absorption or adsorption mechanism. Three basic forms of absorbents are: Synthetic organic sorbents such as Polyurethane foam and Polypropylene fibres; Mineral-based materials such as Perlite and Volcanic ash and Natural Organic materials such as bark, peat moss, hay, feathers, coconut husks and sugar cane waste. This study intends to investigate the use of natural sorbents, particularly sawdust from different woods, to ascertain which displays high absorption capability. Also, to evaluate parameters this could inhibit the absorption process in the system using mathematical tools. Crude oil is a complicated mixture with different chemicals. As a result, the effects of an oil spill on aquatic environment depends on the basic qualities and quantity of the oil spilled as well as the physic-chemical properties off the affected area, [6, 7] . Foe effective clean-up to be achieved, a good knowledge of the physiochemical properties of the hydrocarbon and the nature of the clean-up material is necessary. Besides, products derived from oil are biodegradable and materials of biodegradable form with excellent absorption properties would be beneficial in this operation [8, 9], suggest that these physio-chemical changes enhance oil dissolution in sea water [10]. The effects of pH and modification of adsorbents on Arsenic removal using sawdust and coconut fibers has been carried out [12]. They found out that pH characteristically influenced adsorption process. It was found that maximum adsorption occurred at pH 2 and 12 whereas minimum adsorption took place at p^H 6.8The purpose of this study is to investigate the factors that could inhibit the absorption of crude oil on natural absorbents (sawdust) such as p^H. Hence, the application of a mathematical tool to monitor the rate of absorption with respect to this inhibiting parameter in this study becomes essential [11].

1.0 Theoretical Background

The rate of absorption of this absorbent (biosawdust) with respect to the contaminated environment can be influence by the concentration of their physiochemical parameters. It is of note that the concentrations of these physicochemical parameters influence the rate of bioadsorption. Hence are useful for effective bioremediation. Such properties as the pH, moisture content, NKP etc could influence the bioadsorption of the natural material (sawdust). It is necessary to develop a mathematical model that can simulate the rate of this componenton bioabsorption of sawdust on crude oil contaminated environment.The biomass (sawdust) rate model for the absorption of crude oil in contaminated environment can be formulated as:

$$\frac{d}{dt}(biomass\ in\ the\ sytem) = (rate\ of\ production\ within\ the\ system) \quad (1)$$

which can be written as

$$\frac{dC}{dt} = \beta C \quad (2)$$

Where β = Growth Rate Constant

C = Concentration of biomass

The equation presented is formulated based on the following concept; the rate of adsorption of the contaminant is proportional to the rate of change in the system with respect to time. Therefore, equation (2) can be rearranged in this form

$$\frac{dC}{C} = \beta\, dt \quad (3)$$

Integrating equation (3), we have

$$\int_{C_0}^{C} \frac{dC}{C} = \beta \int_0^t dt \quad (4)$$

$$[\ln C]_{C_0}^{C} = \beta\,[t]_0^t \quad (5)$$

Simplifying equation (5), we have

$$\ln C - \ln C_0 = \beta\,[t-0] \quad (6)$$

$$\ln\frac{C}{C_0} = \beta t \quad (7)$$

Taking the log of both sides of equation (7), we have

$$C = C_0 e^{\beta t} \quad (8)$$

Similarly, from equation (7), β can be expressed as :

$$\beta = \frac{1}{t}\ln\frac{C}{C_0} \quad (9)$$

Substituting equation (9) into (8), we have

$$C = C_0\, e^{\left[\frac{1}{t}\ln\frac{C}{C_0}\right]t} \quad (10)$$

Equation (10) represents the situation when the proportionality constant is positive or increasing. But when a decrease in the functional parameters of interest, the expression becomes

$$\frac{dC}{dt} = -\beta C \tag{11}$$

Applying the appropriate mathematical tools, the equation (11) becomes

$$C = C_0 e^{-\beta t} \tag{12}$$

Where

$$\beta = -\frac{1}{t}\ln\frac{C}{C_0} \tag{13}$$

Substituting equation (13) into (12), we have

$$C = C_0 e^{\left[-\frac{1}{t}\ln\frac{C}{C_0}\right]t} \tag{14}$$

Equation (14) is accepted if there is a decrease in the proportionality constant (β).

Therefore, equation (8) and (14) defines the change in concentration of adsorbent with respect to increase in the functional parameter of interest.

Recalling the first order general equation of Michael Menten's Model, this is:

$$R = \frac{R_{max}[S]}{K_s+[S]} \tag{15}$$

Considering when the specific rate of adsorption R = C, then equation (15) gives

$$C = \frac{C_{max}[S]}{K_s+[S]} \tag{16}$$

We already have:

$$C = C_0 e^{\beta t} = C_0 e^{\left[\frac{1}{t}\ln\frac{C}{C_0}\right]t}$$

Then equation (16) will be expressed as:

$$C_0 e^{\beta t} = \frac{[C_0 e^{\beta t}]_{max}[S]}{K_s+[S]} \tag{17}$$

Substituting the value of β, we have

$$C_0 e^{\left[\frac{1}{t}\ln\frac{C}{C_0}\right]t} = \frac{\left[C_0 e^{\left[\frac{1}{t}\ln\frac{C}{C_0}\right]t}\right]_{max}[S]}{K_s+[S]} \tag{18}$$

Equation (18) is for increasing β, but for decrease in proportionality constant the value becomes:

$$C_0 e^{-\left[-\frac{1}{t}\ln\frac{C}{C_0}\right]t} = \frac{\left[C_0 e^{\left[-\frac{1}{t}\ln\frac{C}{C_0}\right]t}\right]_{max}[S]}{K_s+[S]}$$

3.0 Governing Equation

3.1 Model for pH as an inhibiting factor

The Hydrogen ion concentration of solutions has been known to affect reactions in solutions. The p^H is considered as one of the inhibiting parameter that influences the rate of bio-adsorption. Hence, a mathematical model to describe the p^H inhibitor concept must be considered with respect to increase or decrease in p^H of the reaction as well. Following Michael Menten's equation in terms of reaction rate of inhibiting substrate, we have

$$R = \frac{R_{max}[S]}{K_s + [S]} \cdot I \qquad (19)$$

In terms of pH, it will give

$$R = \frac{R_{max}[S]}{K_s + [S]} \cdot pH \qquad (20)$$

Considering the effect of p^H on the effectiveness of the adsorbent in enhancing bioremediation of a polluted environment , if the rate of absorption is proportional to the rate of change in pH value, then the right mathematical tool to describe it is,

$$\therefore \quad \frac{dpH}{dt} = \lambda\, pH \qquad (21)$$

Where
p^H = Hydrogen ion concentration
t = time
λ = proportionality constant

Equation (21) can be written in this form

$$\frac{dpH}{dt} = \lambda\, dt \qquad (22)$$

Integrating, we have

$$\int_{(pH)_0}^{pH} \frac{dpH}{pH} = \lambda \int_0^t dt \qquad (23)$$

Equation (23) can be expressed as

$$[\ln pH]_{(pH)_0}^{pH} = \lambda\, [t]_0^t \qquad (24)$$

Simplifying (24), we have

$$\ln pH - \ln(pH)_0 = \lambda[t - 0] \qquad (25)$$

$$\ln \frac{pH}{(pH)_0} = \lambda t \qquad (26)$$

Therefore,

$$\lambda = \frac{1}{t} \ln \frac{pH}{(pH)_0} \qquad (27)$$

Express equation (21) in the form of Laplace transform, this to discretize the behaviour of the parameter including its effectiveness, which produces have

$$\frac{dpH}{dt} = S\, pH_s - pH_{(0)} \quad and \quad \lambda pH = \lambda\, pH_s \qquad (28)$$

Substituting equation (28) into (21), we have:

$$S\, pH_{(S)} - pH_{(0)} = \lambda\, pH_{(S)} \qquad (29)$$

Considering the boundary conditions at t = 0, pH(0) = pH_0 (30)

Therefore, substituting the boundary conditions of equation (30) into equation (29), we have:

$$S\, pH_{(S)} - pH_0 = \lambda\, pH_{(S)} \qquad (31)$$

Rearranging equation (31), we have

$$S\, pH_{(S)} - \lambda\, pH_{(S)} = pH_0 \qquad (32)$$

Therefore,

$$(S - \lambda)\, pH_{(S)} = pH_0 \quad (33)$$

Thus,

$$pH_{(S)} = \frac{pH_0}{S - \lambda} \quad (34)$$

The inverse of equation (34) is presented as

$$pH_{(t)} = pH_0 e^{\lambda t} \quad (35)$$

Equation (35) can only be applied when the pH values increases as the rate of absorption is increasing. But if there is a decrease in the rate of the pH value, the proportional constant λ, will be decreasing in the system. Therefore, the differential equation is expressed as:

$$\frac{dpH}{dt} = -\lambda\, pH \quad (36)$$

Using the necessary mathematical tool and conditions, the general solution for equation (36) becomes

$$pH_{(t)} = pH_0\, e^{-\lambda t} \quad (37)$$

And

$$\lambda = -\frac{1}{t} \ln \frac{pH}{(pH)_0} \quad (38)$$

Considering when the rate of adsorption is dependent on the pH, the equation (20) can now be rearranged.

Since, $R_t = pH_t$

$$R = \frac{R_{max}[S]}{K_s + [S]} (pH)_0 e^{\lambda t} \quad (39)$$

In terms of increase in p^H concentration of the developed model, we have

$$C_0\, e^{\lambda t} = \frac{[C_0 e^{\lambda t}]_{max}[S]}{K_s + [S]} (pH)_0\, e^{\lambda t} \quad (40)$$

In terms of decrease in p^H concentration of the developed model, we have:

$$C_0\, e^{-\lambda t} = \frac{[C_0 e^{-\lambda t}]_{max}[S]}{K_s + [S]} \cdot (pH)_0 \cdot e^{-\lambda t} \quad (41)$$

Where

$$\lambda = \frac{1}{t} \ln \frac{pH}{(pH)_0}$$

The equation (39) and (40) becomes:

$$R = \frac{R_{max}[S]}{K_s + [S]} \cdot (pH)_0 \cdot e^{\left[\frac{1}{t} \ln \frac{pH}{(pH)_0}\right] t} \quad (42)$$

$$C_0\, e^{\lambda t} = \frac{[C_0 e^{\lambda t}]_{max}[S]}{K_s + [S]} \cdot (pH)_0 \cdot e^{\left[\frac{1}{t} \ln \frac{pH}{(pH)_0}\right] t} \quad (43)$$

Where

$$\lambda = -\frac{1}{t} \ln \frac{pH}{(pH)_0}$$

Equation (39) and (40) becomes

$$R = \frac{R_{max}[S]}{K_s+[S]} \cdot (pH)_0 \cdot e^{\left[-\frac{1}{t}\ln\frac{pH}{(pH)_0}\right]t}$$

$$C_0\, e^{-\lambda t} = \frac{\left[C_0 e^{-\lambda t}\right]_{max}[S]}{K_s+[S]} \cdot (pH)_0 \cdot e^{\left[-\frac{1}{t}\ln\frac{pH}{(pH)_0}\right]t}$$

Where
R = Rate of reaction
K_s = Micheal Menten's constant
[S] = Hydrocarbon substrate concentration

The rate of P^H function in spillage cleanup exercise has been evaluated through the developed model; the model expresses the influences of p^H on the absorption process through physiochemical properties of the absorbent using selected woody sawdust. The study were able to express the role of p^H in the absorption process, this condition were established through the developed model, the derived model solution has express the behaviour of p^H in the system through the final derived model

CONCLUSION

The behaviour of p^H on the absorption established a relationship through physiochemical properties of the absorbent. Characterizations of selected woody sawdust based on standard and experimental analysis were carried out for p^H. Mathematical model were developed to monitor and evaluate the rate of p^H inhibition on bioabsorption of an absorbent material in the system. Experts will definitely apply the model to examine the behaviour of p^H on the application of sawdust in oil spill clean-up exercise.

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