Journal of the Nigerian Association of Mathematical Physics
Volume 56(**March – May** *2020 Issue*), **pp161 – 164**

KINETICS OF BIO-REMOVAL OF Zn^{2+} FROM SOILS

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Abstract

This is a study on the kinetics of bio-removal of $Zn^{2+}$from contaminated soils using Bacillus subtilis (B. subtilis), Escherichia coli (E. coli), Proteus mirabilis (P. mirabilis); and some mathematical kinetics models. Isolated organisms were cultured and distinctly inoculated in 4g soils conditioned optimally with bio-removal factors in 50 ml beakers. Residual Zn^{2+} was determined on 5, 10, 15, 20, 25, 30and 35days using AAS in triplicate to form data for the kinetics study. The data were fitted within trapaticle diffusion, pseudo first and second order, and elovich models to ascertain the kinetics of Zn^{2+}removal. The models comparison projected the rate-limiting step to be diffusion process, and indicated that the systems were prevailed on by physical process.

***Keywords*:** Zinc, soils, contamination, bio-removal, kinetics

1. Introduction

Expansion of industrialization coupled with fetching resources from under the earth has increased the discharge rate and loads of waste on soils-leading to increased accumulation of heavy metals in media of importance [1]**.** Consequent opon this, the major threats the globe is faced with is soils ladened with hazardous heavy metals in conjuction with harmful chemicals. These substances are of overwhelming, prolonged effects on ecosystem; and they cannot be disintegrated to non-toxic products[2].

In a study conducted by Asha and others in [3], new remediation technogies for handling these toxicants are to be based on pollutant destruction instead of the normal disposal because of their affinity for food chain. Scientific documentation has it that heavy metals are problematic to the systemic functions of human body [4]. Salem and others in [5] added that bisides the fact that some metals at minute concentration are helpful to biological systems, they are also cytotoxic, toxic, mutagenic and carcinogenic in nature when available in high concentration.

According to Kushwaha and others in [6], cobalt, iron, molybdenum, copper and manganese are heavy metals needed in low quantities for the survival and good performances of living organisms; and could be injurious at certain, high concentrations. It is also documented that Mercury, arsenic, uranium, cadmium, silver, nickel, chromium, nickel zinc, selenium and gold are hazardous to the environment if present at concentration above the allowable limits. They are known to adversely impact on soil quality, crop performance and man's health [7, 8].

Physical and chemical solution approaches to metals polluted sites have proven useful but with many after treatment problems- chemical method generates unknown injurious intermediates and end-products in treated soils; and both approaches cannot effect treatment of soils with low concentration of metals[9].

Sulaimon and others stated that some bacteria, yeast, algae and fungi are capable of removing heavy loads of metal ions from soils [10]. This is why bioremediation is preferred to the previously sated methods of cleansing [11]. Bioremediation is a process of removing environmental pollutants or transforming them to halmless products by engaging microorganisms [12].

Motivated by the merits of bio-removal of metals from media, this study focused on the kinetics of bio-removal of zincion from polluted soils at Agbabu Farm Settlement close to mining site in Ondo State by using P. mirabilis, B. subtilis and E. coliand some mathematical kinetics models.

2. Methodology

Soils from contaminated site at Agbabu Farm Settlement was sampled and transported to Microbiology Laboratory in the Department of Microbiology, University of Benin, Benin City where experiment was carried out in the stages of materials sterilization; media preparation; isolation and enumeration of the organisms; and biochemical tests on identification of the organisms as applied in[13].

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Aliquot (0.1ml) each from soil serial dilution was inoculated into different Petri-dishes labelled nutrient and McConkey agars, and the respective media was pured on the aliquot in the petri-dishes [14]. The inoculated plates were inverted and incubated at 37°C and studied for organisms growth at 24 hours [15].Discovered Colonies were counted; recorded [14]; and sub cultured to produce pure culture needed for bio-removal experiments. The bacteria pure culture were characterized and identified using the methods in [16].
The optimal factors (pH, nutrient, temperature, organisms' weights, and stirring frequency) were selected; and the bio-removal tests were conducted on 5, 10, 15, 20, 25, 30 and 35 days of inoculation using the methods in [13, 17]. The amount of metal bio-moved; bio-removed with time; and bio-removed at equilibrium were determined by applying Equations (1), (2) and (3) in [18].

$$q = \frac{(C_o - C_f)}{M}.V \quad (1)$$

$$q_t = \frac{(C_o - C_t)}{m}.V \quad (2)$$

$$q_m = \frac{(C_o - C_m)}{m}.V \quad (3)$$

Where q, q_t,q_m are the metal amount bio-removed in (mg/kg), bio-removed at time t in (mg/kg), bio-removed at equilibrium in (mg/kg); C_o, C_f are the initial Zn^{2+}concentration in (mg/kg), final Zn^{2+}concentration in (mg/kg) after treatment; V is the volume of soil (m^3) exposed to the organisms; and m is the mass (g) of organisms.

The kinetics of bio-removal were analyzed with the models in Table 1. Models' reliability to describe the laboratory data were deduced from the their R^2. High R^2 value indicated that the laboratory bio-removal data could be described by by the fitted model.

Table 1. Names of Kinetic models and their Plot Parameters

S/N	Name of Model	Plot Parameters
1.	Pseudo First Order	$\ln(q_e - q_t)\ vs\ t$
2.	Pseudo Second Order	$\left(\frac{t}{q_t}\right) vs\ t$
3.	Elovich	$q_t\ vs \ln t$
4.	Intra particle diffraction	$q_t\ vs\ (t)^{1/2}$

3. Results and Discussion

The laboratory data were fitted with the selected kinetic models. The fits between ln (q_e-q_t) and t for performance by the different organisms is shown in Figure 1 for pseudo first order. The plots show regression equations and the R^2. The values of K and q_e obtained from the fit are -0.1101$d^{-1}$and 0.1359 mg/kg for B. subtilis; -0.1301d^{-1} and 0.1829 mg/kg for P. mirabilis; -0.1011d^{-1} and 0.07139 mg/kg for E. coli.
The R^2 values were moderate for P. mirabilis and E. coli, and projected that the data could be explained with pseudo-first-order. The R^2 indicated the best fit for Bacillus subtilis with a value of 0.8252, then P. mirabilis with a value of 0.7172 before E. coli with a value of 0.6567. The order of capacity for Zn^{2+}bio-removal shown by K values is E. coli before B. subtilis and then, P. mirabilis.

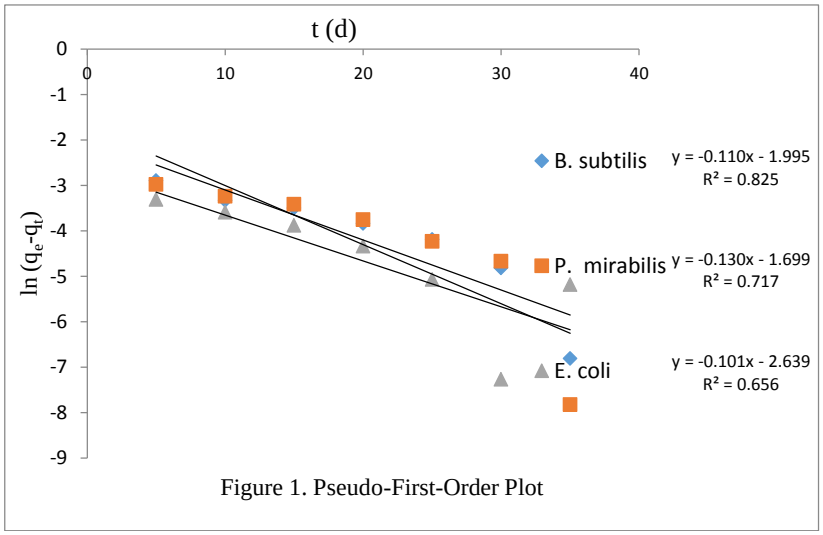

Figure 1. Pseudo-First-Order Plot

The fits between t/q_t and t for the organisms performances are shown in Figure 2 which bears the regression equations and the R^2. The models' R^2 values of 0.6404 is low and showed a fair fit, while the values 0.7926 and 0.6808 for removal by P. mirabilis and E. coli respectively were moderate and showed that the bio-removal data could be fairly explained with pseudo-second-order. The respective K_1 values were 0.0714 kg/mg.d, 0.0264 kg/mg.d and 0.0108 kg/mg.d.

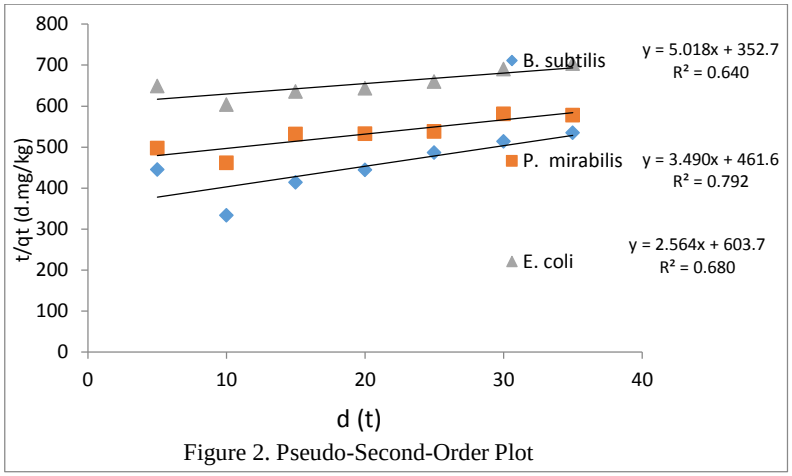

Figure 2. Pseudo-Second-Order Plot

The fits between q_t and ln t for Zn^{2+}bio-removalby the organisms are in Figure 3. The plots displayed the regression equations and the R^2, and the values of α and β were deduced to be 0.0266 $mg.kg^{-1}$ and 37.5939 $mg.kg^{-1}d^{-1}$ for B. subtilis; 0.0253 $mg.kg^{-1}$ and 39.5257 $mg.kg^{-1}d^{-1}$for P. mirabilis; 0.0215 $mg.kg^{-1}$ and 46.5116 $mg.kg^{-1}d^{-1}$ for E. coli.
The high R^2 values of 0.9826, 0.9512 and 0.9561 for removal by B. substilis, P. mirabilis and E. coli respectively indicated that the data could be explained with Elovich model.

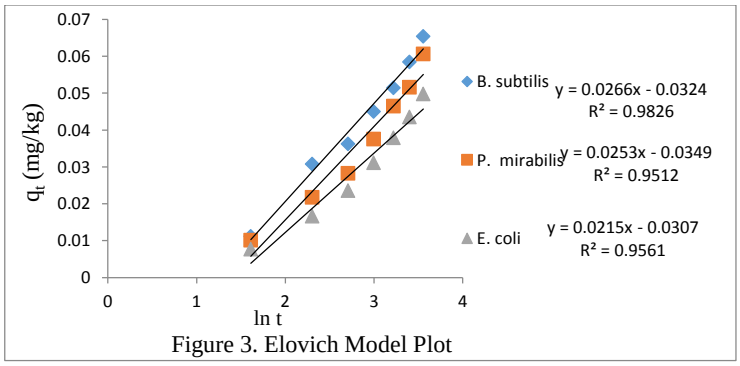

Figure 3. Elovich Model Plot

The fits between q_t and $t^{1/2}$ for the organisms performances are shown in Figures 4 bearing the regression equations and R^2. The K_2value corresponds to the slope. The R^2 values of 0.9876, 0.9913 and 0.9951 for B. subtilis, P. mirabilis and E. coli respectively indicated high correlations, and pointed out that the data could be explained with intra-particle diffusion.
The order of bio-removal capacities indicated by values of $K_2$was B. subtilis, P. mirabilis and E. coli with the respective values of 0.0139 $mg/kg.d^{1/2}$, 0.0135 $mg/kg.d^{1/2}$ and 0.0115 $mg/kg.d^{1/2}$ for K_2.

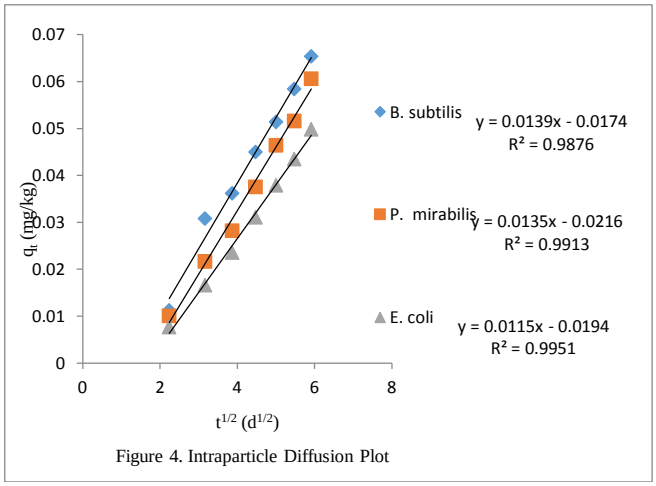

Figure 4. Intraparticle Diffusion Plot

The respective model's R^2 values showed good correlations except the moderate correlations in the cases of pseudo first and second order for E. coli and pseudo second order for B. subtilis. However, the R^2 values comparison in Table 2 showed that the data fitted best into intra-particle diffusion model with R^2 of 0.9876 for bio-removal by B. subtilis, 0. 9913 for P. mirabilis and 0.9951 for E. coli. These implied the rate-limiting step to be diffusion process, and the systems were prevailed on by physical process.

Table 2. Comparing R^2 Values of Models

Kinetic Models	Micro Organisms and Models' R^2 for Zinc Removal		
	B. subtilis	P. mirabilis	E. coli
	R^2	R^2	R^2
Pseudo – First Order	0.8252	0.7172	0.6567
Pseudo- Second Order	0.6404	0.7926	0.6808
Elovich	0.9826	0.9512	0.9561
Intraparticle Diffusion	0.9876	0.9913	0.9951

4. Conclusion

The kinetics models decsibed Zn^{2+}bio-removal by P. mirabilis very well. There was a moderate fit of data with pseudo first and second order for bio-removal by E. coli, and pseudo second order for bio-removal by B. subtilis. The models comparison projected the rate-limiting step to be diffusion process, and the systems were prevailed on by physical process.

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