Study of Arsenic Sorption from Soil Using Selected Microorganisms and Non-Linear Error-Functions Method of Analysis

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ORIGINAL RESEARCH ARTICLE

Abstract- This is a Non-linear approach to kinetic evaluation of arsenic (As) sorption from soil using Microorganisms. Minimization of error functions: average relative error, root-mean-square error, normalized standard deviation and standard error of experiment was applied to compensate for linearizing the non-linear models applied in fitting the laboratory data. The laboratory data was obtained from the study of As removal with cultured indigenous *Klebsiella pneumoniae (K. pneumoniae)* and *Arthrobacter nicotiniae (A. nicotiniae)* used for treating As contaminated soil from Amaonye forest, Ebonye state in Nigeria. Analysis revealed that Arsenic removal by the organisms was reaction-controlled owing to the fact that the removal was dominated by chemical process deduced from pseudo-first-order as highlighted by the minimum ARE value of -2.0324 for *K. pneumoniae* action and -1.9868 for the action of *A. nicotiniae.*

Keywords- Arsenic, microorganisms, sorption, kinetics, error-functions

1 INTRODUCTION

Arsenic (As) belongs to the family of heavy metals (Mukhtar *et al.*, 2017). This family is of very dreaded component members because of their toxic nature when present in media at concentrations above the allowable (Vijaya *et al.*, 2010; Salawu *et al.*, 2014). The challenge of preventing and controlling heavy metals in the environment is global. Environmental decontamination or conservation is a great pursuit of reasonable nations of the world. When nations fail in preventing heavy metals from pilling to objectionable concentration in their environment, they are left with a more expensive alternative of cleaning the environment.

There are different cleaning methods, and these include physical, chemical, and biological. The biological method is further divided into treatment with plants (phytoremediation) and treatment with microorganisms (Girma, 2015; Mukhtar *et al.*, 2017). Bioremediation has come to be preferred to the other methods for its cost effectiveness, efficiency and eco-friendliness (Mukhtar *et al.*, 2017). The mechanisms of bioremediation have been reported to be bio-sorption, biomineralization, bioaccumulation and bio-volatilization (Girma, 2015). The knowledge of these mechanisms is very important for design of feasible remediation systems (Atikpo *et al.*, 2018). Sorption rate of contaminant from media is of principal significance when designing systems for batch sorption (Ho, 2006). For this reason, it is very vital to determine systems time dependence of different conditions of process (Ho, 2006).

Many mathematical models have been developed with time for the study of sorption rate of contaminant from media (Atikpo *et al.*, 2018). Linear regression was extensively used owing to the simple approach involved. Linearized least-square technique with decision-making guide of the coefficient of determination is mostly applicable (Ho, 2006). This method has inherent problems of altered error structure and tempered normality condition. These limitations paved way for the application of non-linear optimization techniques with tools of minimized error function correct the altered normality condition and error structure (Passoss *et al.*, 2008).

Presently, this study looked into the performances of some non-linear kinetic models in their linearized forms and the application of minimized error functions [average relative error (ARE), root-mean-square error (RMSE), normalized standard deviation (NSD) and standard error of experiment (SEE)] to compensate for the linearization of the linearized non-linear models applied in the kinetic of As sorption by *K. pneumoniae* and *A. nicotiniae.*

This study on As sorption is very significant because kinetic study findings will be helpful in designing bioremediation system for As removal from soils, and Amaonye forest soils in particular. Soil is one of the primary means of life (Mukhtar *et al.*, 2017), and arsenic of objectionable concentration is not good in soil. Almost all the organs of human can come in contact with arsenic (Naujokas *et al.*, 2013); even at low quantity, it can lead to many organ damages (Mukhtar *et al.*, 2017). It has many health problems like leucopenia, ataxia, skin disease, renal damage, poor memory, cardiomyopathy, red blood cells destruction, paralysis, jaundice, and inner ear degradation (Arthar and Vohora, 2006). The occurrence of these must be prevented through adequate design requiring proper removal kinetic study.

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2 MATERIALS AND METHODS

2.1 MATERIALS

The materials utilized in this study include: Magnetic stirrer, Filter paper, Hot plate, Cotton wool, Autoclave, inoculating needles, Refrigerator, Pipettes, MacCartney bottles, Beakers, Incubator, Conical flasks, Wire loops, Petrish dishes, Measuring cylinder, Microscope, Atomic absorption spectrophotometer (GBC SensAA, Model no. A6358), and Soil samples.

2.2 REAGENTS

These include: Safranin, Sodium hydroxide, Kovac's reagent, Hydrochloric acid, Oxidase reagent, Sulphuric acids, Methylene blue, Hydrogen peroxide, Crystal violent, Perchloric acid, Ethanol, Nitric acid, and Lugo's iodine.

2.3 NUTRIENTS

These include: MacConkry agar, Kovac's reagent, Nutrient agar, Triple sugar iron agar, Peptone water, Simon citrate ager, and Potato dextrose agar.

2.4 METHOD

The nutrients solutions were prepared with the manufacturers' guide and instruction in (Cheesebrough, 2000). Soil collected from Amaonye forest in Ishiagun was serial diluted. Aliquot (0.1ml) of the dilution (10^{-1}, 10^{-3} and 10^{-5}) was measured into distinct petri-dishes retaining distinct agars (nutrient and MacConkey) using method in (Baron *et al*., 1994) and incubated at 37°C for 24 hours (Cheesebrough, 2000). The developed Colonies were sub cultured and identified using the processes described in Cheesebrough (2000) and Holt (1994).

Requisite bio-sorption factors: organisms' weights (g), pH, nutrient dosage (ml), stirring frequency [per week (pw)]; and temperature (°C), were selected experimentally (Atikpo, and Micheal, 2018). Twenty-four days old *A. nicotiniae and K. pneumoniae* were inoculated respectively in thirty-six (36) 50 ml beakers of 3g of soils each and conditioned with nutrient dosage of 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12ml (Atikpo and Eboibi, 2020). The As residual ion in soil was determined on the fourteenth day using the AAS to ascertain the optimal nutrient after removing the organisms with a centrifuge. The procedure was repeated for 10, 15, 20, 25, 30, 35, 40, 45, 50 and 55°C of temperature; 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10g of organisms' weights; 3, 4, 5, 6, 7, 8, 9, 10, 11 and 12 of pH; and 0, 1, 2, 3, 4, 5 and 6 per week (pw) stirring frequency to ascertain their optimal values (Atikpo and Eboibi, 2020).

The sorption of As by the organisms was studied by weighing 3g of soil into fifteen 50 ml beaker each for each organism. The distinct organisms were inoculated into the respective fifteen beakers of soils and conditioned with the selected optimal factors. This is in accordance with the method in (Atikpo, 2016). The residual As ion was analysed with AAS on the 7th, 14th, 21st, 28th and 35th after a centrifuge action of removing the organisms.

The As removed with time, and at equilibrium were calculated using Equations 1and 2 (Badmus *et al*., 2007).

$$q_t = \frac{(C_o - C_t)}{m}.V \quad (1)$$

$$q_e = \frac{(C_o - C_e)}{m}.V \quad (2)$$

C_0, C_t, C_e, q_t, q_e, V and m are the initial ion in mg/kg; residual ion in mg/kg, remaining ion at equilibrium in mg/kg, amount removed at t in mg/kg, amount removed at equilibrium in mg/kg, volume in m^3 of soil utilized and the mass in gram of the organisms.

The laboratory outputs were subjected to error functions analysis of the non-linear versions fits of intra-particle diffusion, elovich, pseudo-first and second order models presented accordingly in Equation 3 to 6 as stated in (Ho *et al*., 2000; Chien and Clayton, 1980; Mckay and Poots, 1980) to ascertain the kinetics of As ion removal by the organisms.

$$q_t = K_2 t^{\frac{1}{2}} + X \quad (3)$$

$$\frac{dq_t}{dt} = \alpha \exp\left(-\beta q_t\right) \quad (4)$$

$$\frac{dq_t}{dt} = k\left(q_e - q_t\right) \quad (5)$$

$$\frac{dq_t}{dt} = k_1\left(q_e - q_t\right)^2 \quad (6)$$

where q_t is the ion removed by the organism at time t ($mg.kg^{-1}$); k is rate constant of pseudo-first-order (d^{-1}); q_e is the ion removed at equilibrium ($mg.kg^{-1}$); k_1 is rate constant of pseudo-second-order ($kg.\ mg^{-1}d^{-1}$); α is elovich initial rate of ion removal ($mg.kg^{-1}$); β is elovich constant of desorption rate ($mg.kg^{-1}d^{-1}$); and k_2 is the intra-particle diffusion rate constant.

Excel solver add-in was used for the error functions analysis of the laid polynomial relationship between laboratory outputs and time; with minimized objective function at a maximum iteration of one hundred seconds and 0.000001 precision.

3 RESULTS AND DISCUSSION

Conducted microbiology analysis (biochemical tests) as recommended in (Cheesebrough, 2000; Holt *et al*., 1994) revealed *A. nicotiniae and K. pneumoniae* from the analysed respective colony of 4.2×10^2 and 1.6×10^6 as presented in Table 1. Bio-sorption factors analysis revealed optimal performance factors of 6 ml (nutrient dosage), 35°C (temperature), 1g (organism's weight), 7 (pH), and 6pw (stirring frequency) for *A. nicotiniae* (Atikpo and Eboibi, 2020); and 10 ml (nutrient), 35°C (temperature), 5g

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(organism's weight), 7 (pH) and 6pw (stirring frequency) for *K. pneumoniae* (Atikpo and Eboibi, 2020)

Laboratory data of As removal by the applied organisms were studied with the linear versions of the selected kinetic models and scrutinized with error functions (RMSE, SEE, ARE and NSD) in their minimized conditions. This was directed at determining the removal control processes that are deducible from the rate-controlling steps of the removal using mathematical kinetic models. In this study approach, As removal by *K. pneumoniae* was discovered to be reaction controlled as the removal was dominated by chemical process. This was deduced from the minimum ARE value of -2.0324 as compared with the minimum values of 0.000539, 0.000140, and 1.4607 for RMSE, SEE and NSD respectively. The minimum (-2.0324) for ARE picked on pseudo-first-order; while the minimum values of RMSE, SEE and NSD picked on intraparticle diffusion, elovich and intraparticle respectively as shown in Table 2. Judging from the presentation above, the minimum error function reflected chemisorption rate limiting and a reaction-controlled removal.

The information from error function computation on *A. nicotiniae* action revealed a greater exerted influence by *A. nicotiniae* than *K. pneumoniae* influence. The minimum -1.9868 of ARE is indicative that the action of *A. nicotiniae* was chemical controlled with chemisorptive rate limiting deduced from pseudo-first-order. This was recognized from the minimum value of ARE compared with 0.000478 of RMSE, 0.000106 of SEE and 0.4424 NSD as shown in Table 3. RMSE and NSD highlighted intraparticle diffusion, while SEE picked the elovich model.

4 CONCLUSION

This is a study of Arsenic (As) sorption using *A. nicotoniae* and *K. pneumoniae* and non-linear kinetic approach. Some error functions: ARE, RMSE, NSD and SEE were engaged to compensate for linearizing the non-linear models used. Arsenic removal by the organisms was reaction-controlled owing to the fact that the removal was dominated by chemical process deduced from pseudo-first-order as highlighted by the minimum ARE value of -2.0324 for *K. pneumoniae* action and -1.9868 for the action of *A. nicotiniae*. This study will be useful for planning and design of As sorption by the organisms from the soils. It will also serve as a reference for similar study in the future.

Table 1. Identification of organisms

Cultural Morphology	Biochemical Tests									Bacteria Isolates
	Gram reaction	Catalase	Oxidase	Indole	Citrate	Glucose	Lactose	H_2S	Motility	
Creamy and raised colonies on agar plates	GNR	+	-	-	+	+	+	-	-	*Arthrobacter nicotiniae*
Creamy mucoid and ovoid and discrete on agar plates	GNR	+	-	-	+	+	-	-	-	*Klebsiella pneumoniae*

Note: GNR = Gram Negative Rods (Bacilli), (+) = positive, and (-) = negative.

Table 2. Summarized error functions computation for removal by *K. pneumoniae*

Error Function	Pseudo-First-Order	Pseudo-Second-Order	Elovich	Intraparticle Diffusion	Best Model Selected
SEE	0.0939	0.000176	**0.000140**	7.9870	Elovich
NSD	7.4949	3.1191	2.6407	**1.4607**	Intraparticle Diffusion
ARE	**-2.0324**	-0.8646	0.7281	0.4006	**Pseudo-First-Order**
RMSE	0.4798	0.00117	0.000984	**0.000539**	Intraparticle Diffusion

Table 3. Summarized error functions computation for removal by *A. nicotiniae*

Error Function	Pseudo-First-Order	Pseudo-Second Order	Elovich	Intraparticle Diffusion	Best Model Selected
SEE	0.0802	0.000698	**0.000106**	5.5366	Elovich
NSD	7.1946	4.9843	0.8421	**0.4424**	Intraparticle Diffusion
ARE	**-1.9868**	-1.4070	0.2289	-0.1346	**Pseudo-First-Order**
RMSE	0.4510	0.00462	0.000715	**0.000478**	Intraparticle Diffusion

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