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Isotherms and batch kinetics of the biosorption of cadmium onto pre-treated tridax procumbens

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ABSTRACT

The ash obtained from Tridax procumbens leaves was used to adsorb cadmium from aqueous solution of Cadmium chloride. The sorption process with respect to its metal ion concentration, pH, contact time and particle size on adsorption were studied. The percentage removals with respect to the parameters were also studied. The most effective pH range was found to be 5.8-6.0 for sorption of metal ions. The first order rate equation by Lagergren was tested on the kinetic data and the adsorption process followed first order rate kinetics. Isotherms data were analyzed for possible agreement with Langmuir and Freundlich adsorption isotherms; the model for dynamics of metal ions uptake proposed in this work fitted the experimental data reasonably well for Freundlich adsorption isotherm than Langmuir adsorption isotherm. The correlation coefficients (R^2) were 0.998 and 0.912 for Freundlich and Langmuir isotherms respectively.

Key Words: Biosorption, Isotherms, Cadmium, Tridax procumbens, Synthetic waste water.

INTRODUCTION

The presence of heavy metals in aquatic environment is known to cause severe damage to aquatic life, beside that these metals kill microorganisms during biological treatment of waste water with a consequence delay of the process of water purification. Industrial and mining waste water are the major sources of pollution by heavy metals. These industrial activities can generate a considerable pollutional stress in the ecosystem. Heavy metals can pose health hazards to man and the aquatic lives if their concentrations exceed allowable limits. Concentrations of heavy metals below these limits even have potential for long-term contamination [1, 2]. Cadmium which is widely used and extremely toxic in relatively low dosage , is one of the principal heavy metals responsible for kidney damage, renal disorder, high blood pressure, bone fracture and destruction of red blood cells [3, 4]. The main anthropogenic pathway through which cadmium

(II) enters the water bodies is via waste from industrial processes such as electroplating, metallurgical processes, plastic manufacturing etc [4, 5, 6]. The commonly used methods for removal of metal ions from waste water include, precipitation, coagulation/flocculation and ion exchange [7, 8, 9]. These methods have been reported to be expensive and also have disadvantage of incomplete metal removal, high reagents and energy cost and generation of waste product that require proper disposal [10]. Thus preparation and use of environmentally friendly materials for adsorption is desirable.

Adsorption of heavy metal ions onto activated carbon has been applied widely as a unit operation in the treatment of industrial waste water [10, 11, 12]. Activated carbon has been reported to have high and fast adsorption capacities due to its well developed-porous structure and tremendous surface area [13]. The use of commercial activated carbon is not suitable for developing country like Nigeria due to high cost. Therefore there is need to produce activated carbon from cheaper and readily available materials which can be used commercially on a large scale.

Activated carbon from agricultural waste products such as rice husk, groundnut husk, coconut shell, various seed shells etc have been used effectively for the adsorption of heavy metals in waste water [6, 14, 15, 16, 17]. In this study Tridax procmbens leaves for the first time is converted to ash and is applied for the removal of cadmium (II) from synthetic industrial waste water.

MATERIALS AND METHODS

Preparation of Adsorbent

Tridax procumbens leaves were collected from various locations in Gwagwalada, Abuja in the month of October. The leaves were first washed with tap water then rinsed with deionised water and sun dried for 14 days. The leaves were then grounded with electric grounder. After been grounded the leaf particles were sieved using different sieves with different particle sizes such as 0.063mm, 0.212mm, 0.425mm, and 2.0mm. The sieved particles were dried at 100^{o}C for 24 hours. The ash was stored in the desiccator until used.

Batch Adsorption Studies

Batch experiment was conducted at ambient temperature using optimum conditions of factors that influenced adsorption such as initial concentration, pH, contact time and particle size. Stock solution of cadmium (1000mg/L) was prepared by dissolving cadmium Chloride in distilled water. The pH of the solution was adjusted by using 0.1N NaOH and/or 0.1N H_2SO_4. The concentration range of Cadmium prepared from stock solution varied from 100mg/L to 500mg/L.

The experiments were conducted in the batch system for measurement of adsorption capacities. Each Cadmium solution was placed in series of 250ml flasks and known amount of adsorbents (2g) were added to each flask. The flasks were clamped on a mechanical shaker and agitated for 60 minutes. After agitating the solution and biosorbent, the biosorbent was removed by filtration using Whatman filter paper. The residual cadmium ion concentrations in the filtrate (after adsorption) was measured by atomic adsorption spectrophotometry (Model AA320N) using airacetylene flame at wavelength of 228.8nm. Adsorption equilibrium was calculated by using the following equation:

$$q_t = (C_i - C_f)V/m \qquad (1)$$

where C_i and C_f are the Cd (II) concentrations in mglL initially and at given time, t, respectively. The percentage removal of Cd (II) from solution was calculated using the following equation:

$$R_{Cd(II)}(\%) = C_i - C_f/Ci \times 100 \qquad (2)$$

Finally the suitability of the Freundlich and Langmuir adsorption models to the equilibrium data were investigated for Cadmium-sorbent system.

RESULTS AND DISCUSSION

Effect of pH

The experiments carried out at different pH (2-10) indicate that Cadmium (II) removal from aqueous solution by the adsorbent is dependent on the pH of the solution (Figure 1). The pH is related to surface charge of the adsorbent and degree of ionization [10, 18].

The effect of pH was carried at the predetermine initial ion concentration (100mg/L), adsorbent dose (2.0g/100cm^3), contact time (60mins) and particle size (0.063mm) and varying pH value (2 – 10) using NaOH or H_2SO_4 as appropriate. There was an increased in percentage removal with increased pH from 2-6. At a pH value of 6, the percentage removal becomes a maximum as shown in Figure 1. Above pH value of 6, there was a reduction in percentage removal. The biosorption of Cadmiun in highly acidic medium (pH1) was observed to be negligible due to the competition of hydrogen ions for the active sites [10, 11]. As the pH increases there is increasing trend in concentration of hydroxide ion (OH-) in solution, there by causing shift in the equilibrium. Hence, the systems adjust to terminate this effect (Le Chatelier principle) by precipitation of hydroxide out of the solution. At low pH value, there was reduction in removal efficiency of the metal ion. This may be as a result of the presence of hydronium ions (H_3O^+) on the surface of the adsorbent, which caused respulsion of the metal ions to the surface functional groups and consequent reduction in the removal efficiency of the metal ion by the adsorbent [10].

Effect of Initial Concentration on Sorption by the Sorbent

initially Cadmium (II) percentage removal by the adsorbent increased rapidly with increasing Cd concentration and slowed down when Cd concentration reached 500mg/L as shown in Figure 2. At lower concentration, Cd ion in the solution would interact with the binding sites and does facilitate adsorption. At higher concentration, more Cd ions are left unabsorbed in solution due to the saturation of binding site. Maximum removal (74%) of Cd ions was achieved when 500ppm Cd (II) concentration was adsorbed with 2.0g/100cm^3. In this study the concentration of Cd that will attain higher percentage removal of Cd (II) was 500ppm at 60 minutes of treatment.

Effect of Contact time on Metal Sorption by Adsorbent

Figure 3 shows the percentage removal of Cadmium as functions of contact time. This is also an important parameter for an economical waste water treatment. The figure shows that the sorption process increased with increased contact time until maximum was attained at 100minutes. This was attributed to the instantaneous utilization of the most readily available sorbing sites on the adsorbent surface. Increased contact time increased percentage removal of Cadmium until equilibrium was established.

The equilibrium adsorption was established within 100 min and the kinetic data was fitted to the Lagergren equation [10, 19, 20, 21] .

$$\mathrm{Log}(Xe - X) = \mathrm{Log}(Xe - Kads)t/2.303$$

X = the amount of Cd ion removed at time t, Xe = amount removed at equilibrium and Kads = the rate constants of adsorption. The plots of Log(Xe – X) versus t show the applicability of the above equation for the metal sorption by the adsorbent .The rate constant of adsorption (k_{ads}) was calculated to be 6.3×10^{-2} minutes which indicates that it is a first order kinetics.

Effect of Particles size of the Adsorbent on Sorption of Metal

Various particle sizes of the adsorbent such as 0.63mm, 0.21mm, 0.43mm, 0.60mm and 2.00mm were used in the adsorption experiment. The percentage removal of the Cadmium ion at different particle sizes showed that the percentage removal rate increased between particle sizes of 0.063mm and 0.600mm where the maximum adsorption was recorded (Figure 5). Below 0.60mm the percentage removal rate decreased sharply down to particle size of 2.0mm (figure 5). The higher adsorption level achieved by smaller particle size of the adsorbent may be connected to the fact that smaller particles give larger surface area. There is a tendency that smaller particle size produced shorter time to equilibrate [10].

ADSORPTION ISOTHERM

Adsorption isotherm models were widely employed to show the relationship between the equilibrium solute concentration in bulk solution and its amount adsorbed per unit of adsorbent at constant temperature. The equilibrium data obtained from Cadmium sorption capacity of adsorbent were fitted to langmuir and Freundlich isotherms.

Freundlich Adsorption Isotherm

The linearized form of freundlich adsorption isotherm was used to evaluate the relationship between the concentration of Cd adsorbed by the adsorbent and Cd equilibrium concentration in wastewater, and is given as

$$\ln C_a = \ln k + 1/n \ln C_e$$

where C_a is the amount adsorbed, C_e is the equilibrium concentration and k and 1/n are empirical constants incorporating all the parameters affecting the adsorption process. Parameters k and 1/n are respectively equal to intercept and slope and were determined to be (0.2 and 0.5) respectively as shown in Figure 5. The correlation coefficient $R^2 = 0.998$.

According to [12] a larger value of k indicates good adsorption efficiency for a particular adsorbent, while a larger value of 1/n indicates a larger change in the effectiveness in adsorbent over different equilibrium concentrations.

Langmuir Adsorption Isotherm

The linearized Langmuir adsorption isotherm allows the calculation of adsorption capacities and the Langmuir constants as given by the following equation

$C_{eq}/q = 1/qmax.b + C_{eq}/q_{max}$

Where q is milligram of metal accumulated per garm of the adsorbent material; C_{eq} is the metal residual concentration in solution; q_{max} is the maximum specific uptake corresponding to the site saturation; b is the ratio of adsorption and adsorption rate. The linear plots of C_{eq}/q against C_{eq} indicate that adsorption follow the Langmuir model (Figure 6). The parameter qmax and b were determined as slopes and intercept of the plots and were found to be 0.069mg/g and 1.1L/mg in respectively. The correlation coefficient $R^2 = 0.912$. When the initial metal concentration raises adsorption increases while the binding sites are not saturated.

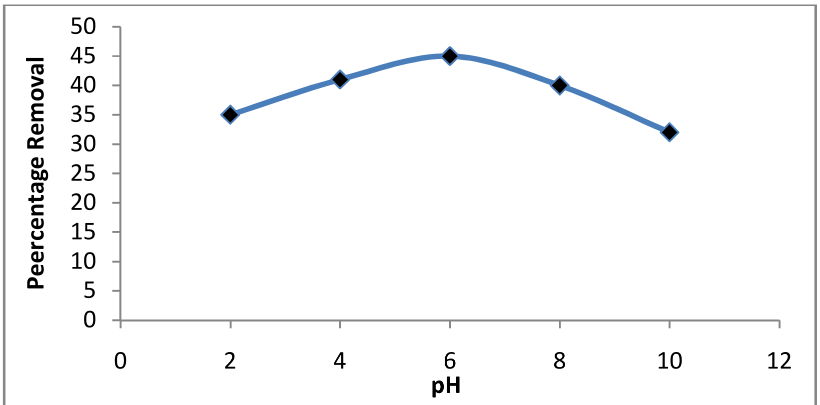

Figure 1: Effect of pH

CONCLUSION

The adsorption analysis carried out in this study showed that tridax procumbens have adsorption capacity for the removal of Cd (II) ion in wastewater. The optimum conditions of Cd (II) ion uptake by the adsorbent were; initial metal ion concentration of 500mg/L, pH value of 6, contact time of 100 minutes and particle size of 0.60mm. The first order rate equation by Lagergren was tested on the kinetic data and the sorption process followed first order kinetics. The rate constant of adsorption (K_{ada}) was found to be 6.3×10^{-2} minutes

In this study, the correlation coefficient for freundlich isotherm R^2 was found to be 0.998 and that of Langmuir isotherm was 0.912.This indicates that freundlich isotherm had a better fitting model than Langmuir isotherm.

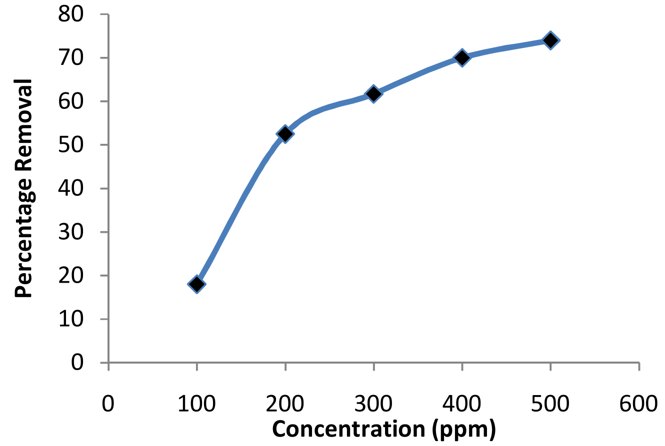

Figure 2: Effect of concentration

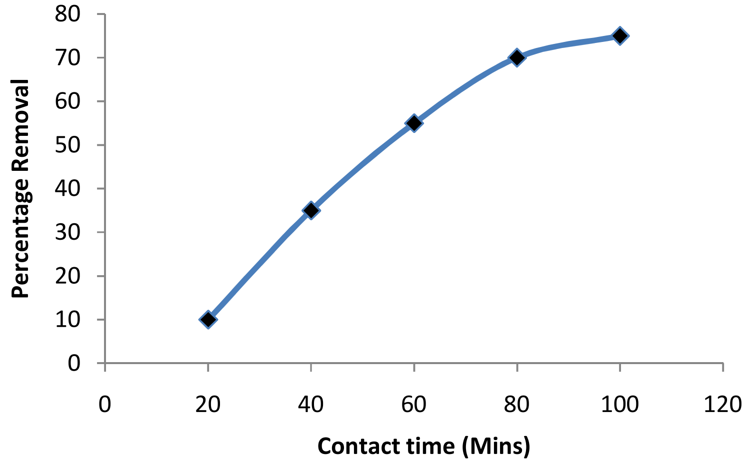

Figure 3: Effect of contact time

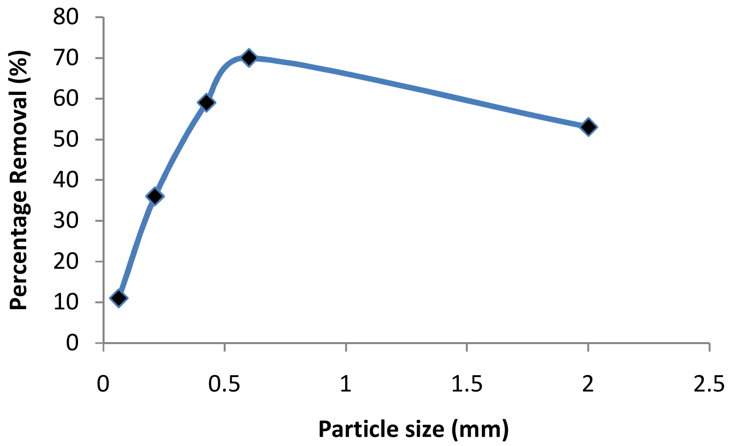

Figure 4: Effect of perticles size

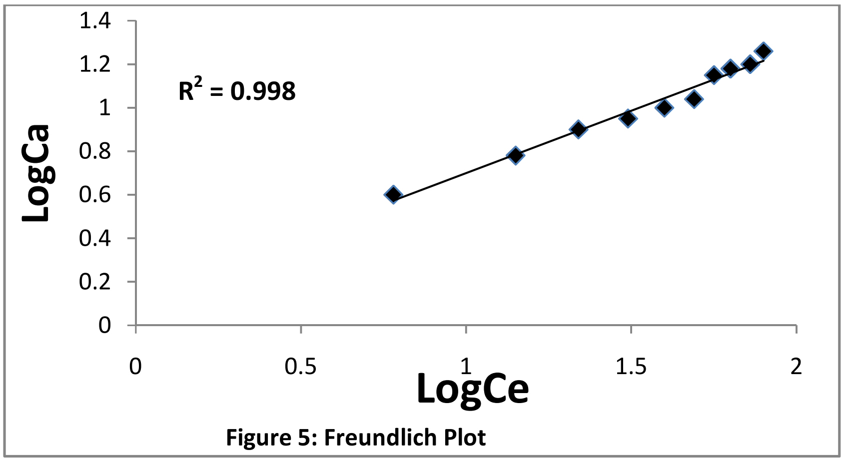

Figure 5: Freundlich Plot.

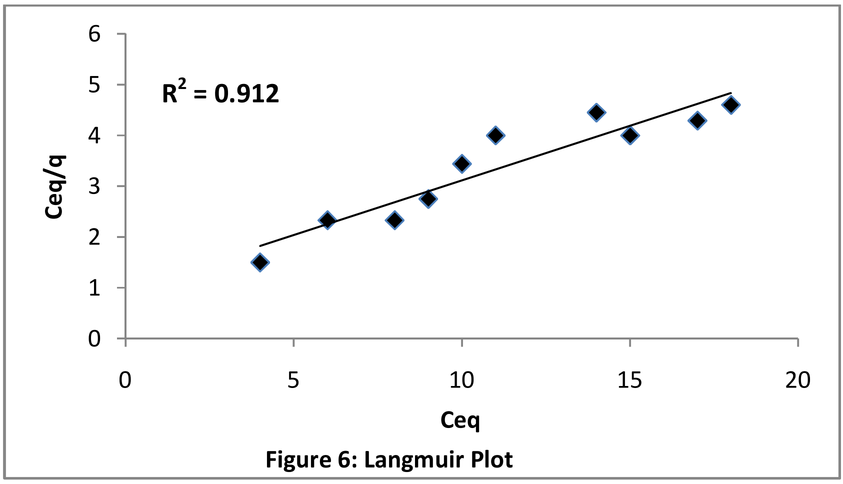

Figure 6: Langmuir Plot.

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