Adsorptive Removal of Atrazine from Aqueous Solution Using Bambara Groundnut Hulls (*Vigna Subterranean*)

E. Sebata*, M. Moyo, U. Guyo, N. P. Ngano, B. C. Nyamunda, F. Chigondo, V. Chitsa, M. Shumba
Department of Chemical Technology
Midlands State University
Gweru, Zimbabwe

Abstract

The removal of atrazine from aqueous solution was performed using bambara groundnut hulls powder as a biosorbent by batch adsorption studies. The operating variables studied were pH, adsorbent dosage, contact time, initial concentration and temperature. The adsorption process was found to be highly pH dependent, with pH 7.0 being optimum. The biomass required at saturation was 0.9 g and the equilibrium was reached after 120 min. The Freundlich isotherm equation fitted the equilibrium data for atrazine sorption. The Q_{max} and K_f values were found to be 3.5236 mg/g and 0.3221 mg/g respectively. The aforementioned parameters indicated that bambara groundnut hulls could be used as a new and efficient adsorbent material for the removal of atrazine from wastewaters. The equilibrium isotherm was found to be pseudo first order with an equilibrium constant of 0.01313 min^{-1}. Desorption experiments were carried out and the desorption percentage ranged from 45 to 70%

1. Introduction

Environmental contamination due to the excessive use of pesticides has become a great concern to the public and to environmental regulatory authorities worldwide. In Zimbabwe, extensive industrial and agricultural activities results in the production use of organochlorine and organophosphorous pesticides. The pesticides are some of the major pollutants of the surface and groundwater resources. They are harmful to organisms even at μgL^{-1} levels and as a result, are considered as pollutants of major concern [1]. Pesticides are some of the major agricultural inputs used to destroy insects or other organisms that are harmful to plants, thus increasing the agricultural yield. However, continuous use of these has resulted in many environmental problems [2].

Atrazine (2-chloro-4-(ethyl amino-6-isopropyl amino)-1,3,5-triazine) (see Figure 1) belongs to a chlorinated triazine group of herbicides and is one of the widely used pesticides in the world. It is used for the control of grassy and broadleaf weeds in sorghum, corn, pineapple, maize, wheat, soya bean, macadamia nuts, sugarcane and many other crops [3,4]. Despite the fact that it has been banned in many European countries, it is still widely used as a herbicide in Zimbabwe.

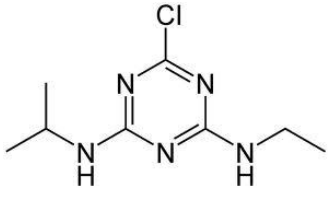

Figure 1: Structure of atrazine

Introduction of atrazine to the environment occurs during its formulation, manufacture and disposal. It may also enter the atmosphere during application in the form of dust particles that contain atrazine. In the atmosphere, atrazine exists in both the particulate and vapor phases due to its low vapor pressure. These forms influence how atrazine is transported or later deposited into aquatic environments [5].

Atrazine may also be removed from the soil by surface runoff and through seepage into

groundwater. It persists in surface and groundwater, with a tendency to bind onto sediments [6]. The degradation in surface waters is slow. It is almost nonvolatile with a half-life in neutral conditions of about 200 days, but varies from 4-57 weeks depending on various environmental factors. Atrazine is commonly found in surface and ground waters because of low degradability [7].

Exposure to high levels of atrazine may cause irritation of eyes, skin and mucous membranes. High doses in animals and humans can cause damage to the heart, kidney and liver. Atrazine is capable of disrupting the immune system. Maternal exposure to atrazine herbicides in drinking water is associated with increased incidences of developmental effects in newborns, including low birth weight, heart, urinary and limb defects [8]. Increased rates of premature delivery have been observed for couples living on farms that use atrazine [9]. Human miscarriages have been observed to increase in women exposed to atrazine. Exposure to high levels of atrazine in men results in reduced sperm quality, decreased sperm motility and prostate inflammation. Due to its ability to disrupt the endocrine system and interfere with hormones, atrazine has been linked to limb deformities and weakened immune systems. [10].

The main public health concerns about the application of atrazine are the claims regarding hormone and reproductive disruptive effects and its links to cancer. It is linked to ovarian tumours, breast and testicle tumors. Atrazine breaks down to hazardous substances and produces dangerous synergistic effects [11,12].

Several conventional methods have been reported for atrazine removal from soil, water and wastewater. These include chemical treatment, incineration, adsorption, phytoremediation and biodegradation. Most commonly employed chemical methods for the remediation of atrazine bearing wastewaters are hydrolysis, photolysis, oxygenation and dehalogenation. These methods are either very costly, produce other toxic substances or are not feasible hence the need for a cheaper method [13.

In recent years, much attention has been directed to biosorption as a new technology. The method is based on the binding capacities of various biological materials. Biosorption is the ability of biological materials to accumulate waste from wastewater through metabolically mediated or physicochemical pathways of uptake [14]. Biological materials from agricultural wastes, algae, bacteria, fungi and yeasts have proved to be potential biosorbents [15]. The advantages of biosorption as a wastewater treatment method are its high efficiency, low cost, minimized chemical and biological sludge, biosorbent regeneration and that no additional nutrients are required. [16].

Biosorption process involves a solid phase and a liquid phase containing a dissolved species to be sorbed (in this case the pesticide). Due to the higher affinity of the sorbent for the sorbate species, the latter is attracted and bound to the former by different mechanisms. The process continues until equilibrium is established between the amount of solid-bound sorbate species and the portion remaining in the solution. The degree of sorbent affinity for the sorbate determines its distribution between the solid and liquid phases [17].

The regeneration of biosorbent may be important in keeping the process costs down and in opening the possibility of recovering the materials extracted from the liquid phase. For this purpose it is desirable to desorb the sorbed materials and to regenerate the biosorbent material for another cycle of application [18]. The desorption process should not cause any physical changes or damage to the biosorbent, yield the organic material in a concentrated form, and restore the biosorbent close to the original condition for effective reuse.

This study seeks to determine whether bambara groundnut hulls can be effectively used in reducing the amount of atrazine from aqueous solutions. Bambara groundnut seed hulls are readily available in large quantities and may present a high potential as inexpensive sorbents for water treatment. The use of bambara groundnut hulls can be environmentally friendly and may promote green chemistry [4]

2. Materials

Reagents

Sodium hydroxide (Sarchem), nitric acid (Sigma Aldrich), formaldehyde (Merck), acetone, uranine (Merck), hydrochloric acid (Merck), atrazine (Sigma Aldrich).

Instrumentation

Fourier transform infra-red spectrophotometer (FT-IR) (Digilab Merlin Samitar) and a UV-Vis spectrophotometer (UV-1601 Shimadzu Japan)

3. Methods

3.1. Sampling and preparation of the biomass (bambara groundnut hulls)

Bambara groundnuts were collected from a local farm in Nyamandlovu, Zimbabwe and were shelled. The hulls were washed thoroughly with distilled water in order to remove impurities and air dried. The bambara hulls were then oven dried at 80^{o}C to a constant mass [19]. They were crushed and sieved to a particle size of 300 µm. Nitric (0.1 M) acid was used for the acid treatment by soaking the bambara groundnut hull powder for 24 h to increase its sorption capacity. 20 grams of biosorbent per litre of solution was used and the mixture was filtered. The powder residue was washed with distilled water to remove all the acid. Washing was done several times until the pH of the filtrate was neutral [20]. The filtered biomass was dried at room temperature and dried in an oven at 105°C to constant mass. The biomass was then stored in a desiccator [21].

3.2. Characterization of biosorbent

FTIR spectroscopy was used to identify the functional groups on the bambara groundnut hull. This was carried out on the treated biomass before and after biosorption. The samples were prepared by diluting the adsorbent to 5% in KBr and cast into disks for analysis [22].

3.3. Preparation of stock solutions and reagents

1.68 mL of 50% atrazine was dissolved in a small amount of acetone. 1000 ppm stock solution was then prepared by making up to the mark of a 1000 mL volumetric flask with distilled water [21].

3.4. UV-Vis analysis of atrazine

In each case, 5 mL of the filtrate were reacted with 0.5 ml of uranine dye (10 ppm) and pure formaldehyde (1 mL). The absorbance was then measured using distilled water as the blank at 225 nm [23].

3.5. Equilibrium adsorption experiments

Batch experiments were carried out to determine the optimum conditions for the equilibrium biosorption of atrazine by the bambara groundnut hulls. The parameters investigated were the effect of pH, biosorbent dosage, contact time, temperature and initial concentration. The atrazine concentration retained in the adsorbent phase was calculated according to mass balance of the equation 1:

$$Atrazine\ uptake,\ \ Q_e = V\frac{(C_o - C_e)}{W} \qquad (1)$$

Where: C_0 and C_e are the initial and equilibrium concentration (mgL^{-1}) respectively of atrazine in solution, V is the volume of atrazine in solution (L), and W is the mass (g) of the adsorbent.

The amount of atrazine removed was calculated using equation 2

$$\%\ Atrazine\ removed = 100\ \frac{(C_0 - C_e)}{C_o} \qquad (2)$$

3.5.1. Effect of pH

The effect of pH on the amount of atrazine removal was analysed between the pH range of 1.0 - 9.0. 50 mL of 50 mgL^{-1} atrazine solution was transferred into a stoppered conical flask containing 0.5 g of bambara groundnut hulls. The mixture was agitated (150 rpm) at room temperature for 24 h. The samples were centrifuged and the supernatant solution filtered. The sample was analysed using the UV-Vis spectrophotometer. Adjustment of pH was done with HCl and NaOH

3.5.2. Effect of Contact Time

Optimisation of contact time between the solution and bambara groundnut hulls surface was perfomed by contacting 0.5 g of the adsorbent with 50 mL of 50 mgL^{-1} atrazine solution for 15 to 150 min. The pH was maintained at 7. The samples were removed from the rotary shaker and centrifuged. The supernatant solution was analysed using the UV-Vis spectrophotometer

3.5.3. Effect of Biomass Dosage

50 ml of 50 mgL^{-1} atrazine solutions were contacted with different masses of bambara groundnut hull ranging from 0.1 to 1.4 g. The pH was maintained at 7 and each sample was then agitated for 120 min at 150 rpm. The samples were centrifuged and the concentrations were then analysed for atrazine using the UV-Vis spectrophotometer [22].

3.5.4. Effect of temperature on biosorption of atrazine

Adsorption experiments were carried out at 20, 25, 30, 40, 50 and 60 ^{o}C. For each sample 50 mL of 50 mgL^{-1} atrazine solutions were contacted with 0.9 g of bambara groundnut hull. Each sample was then agitated for 120 min at 150 rpm. The samples were then centrifuged and the supernatant was analysed for atrazine using the UV-Vis spectrophotometer [22].

3.5.4. Effect of Initial concentration

Effect of initial concentration was studied at varying initial concentrations (10-70 mgL^{-1}). pH was adjusted to 7 and 0.9 g of biosorbent was used. Agitation was done with a rotary shaker set at 150 rpm for 120 min, followed by filtration and analysis for remaining atrazine with the UV-Vis spectrophotometer [24

3.6. Kinetic studies

50 mL of the sample was added to a conical flask containing 0.9 g of biosorbent. The flasks were shaken at 150 rpm on a rotary shaker. For the first 10 min, samples were collected at 1 minute intervals followed by 10 min interval collection for 120 min. Samples were filtered and analysed for atrazine

3.7. Desorption studies

Desorption studies were carried out using the exhausted adsorbents. The adsorbents with varying concentrations of atrazine (7.8-31.0 mg/L) were used. Each adsorbent was placed in 300 mL of 5% (v/v) methanol in distilled water and was shaken for 120 min at150 rpm. The sample was filtered and analysed for the amount of atrazine desorbed. The desorption ratio was calculated [4].

4 Results and discussion

4.1. FTIR Characterisation of bambara groundnut hulls

The FTIR spectra of the bambara groundnut hull before and after sorption are shown Figure 2. A broad peak at 3415 cm^{-1} is the indication of -OH and –NH groups. The stretching of the -OH groups bound to methyl radicals is attributed to a signal at 2921 cm^{-1}. The peaks at 1736 and 1635 cm^{-1} are characteristic of carbonyl group stretching from aldehydes and ketones. The presence of -OH group, along with carbonyl group, is attributed to the presence of carboxylic acid groups in the biosorbent. The peak observed at 1050 cm^{-1} is due to C-O bonds.

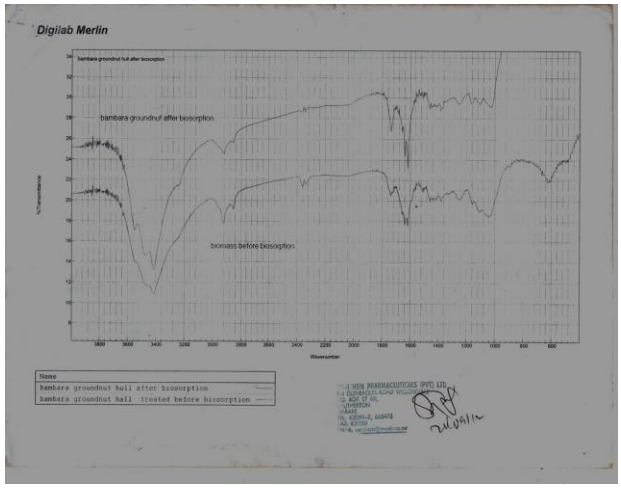

Figure.2: FTIR spectra of bambara groundnut hull before and after biosorption

The hydroxyl, carbonyl and carboxylic acid groups are important sorption sites [25]. After biosorption there was a shift and broadening of adsorption peaks. The shift of the OH peak from 3415 to 3448 cm^{-1} indicates the involvement of the hydroxyl groups in the adsorption of atrazine. The shifting of the carbonyl group peak from 1635 to1660 cm^{-1} also shows that the carbonyl groups participated in the adsorption of atrazine. The results of the FITR spectrum show the participation of carbonyl and hydroxyl groups of bambara groundnut hull as active binding sites for the adsorption of atrazine.

4.2. Batch studies

The investigation of the efficacy of atrazine uptake by the biosorbents is essential for the industrial application of biosorption, as it gives information about the kinetics of the process which is necessary for the design of the equipment. The atrazine uptake is usually measured by the parameter 'Q_e' which indicates the mass (mg) of atrazine accumulated per mass (g) of biosorbent material.

4.2.1. Effect of pH on biosorption of atrazine

pH is an important parameter in biosorption as it affects both the degree ionisation of the sorbate and the surface charge of the sorbent during the biosorption process. pH influences biosorption by a way of modifying the functional groups of the bambara groundnut hull biosorbent. Figure 3 shows the effect of pH on the adsorption of atrazine. The amount adsorbed was almost constant between pH 6 and 8, and a maximum adsorption of 1.93 mg/g (77%) was obtained at pH 7. Treatment of the bambara groundnut hulls with nitric acid developed acidic surface sites which had a high affinity for the basic atrazine and hence the ability to remove atrazine [26]. The results are in agreement with findings by Chaparadza and Hossenlopp, [27] who found that the removal of atrazine from aqueous solution by charred banana peels was maximum at about pH 7.

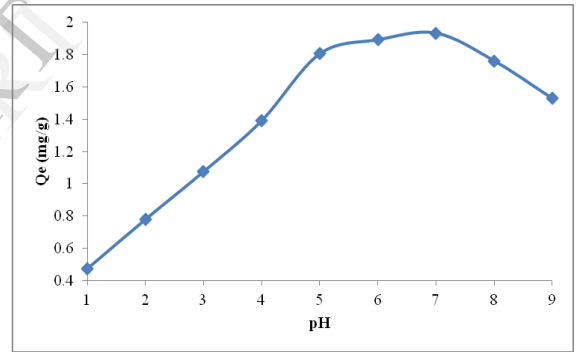

Figure 3: Effect of pH on biosorption of atrazine

4.2.2. Effect of contact time on bisoprtion of atrazine

The effect of contact time on biosorption of atrazine was investigated from 15-150 min. Figure 4 shows the effect of contact time on the adsorption of atrazine. The removal rate of atrazine increased with an increase in contact time. The rate of adsorption is higher in the beginning due to a large available surface area of the biosorbent. The fast initial uptake is also due to the rapid accumulation of atrazine on the surface of the adsorbent. As these sites become exhausted the uptake rate will be controlled by the rate at which the adsorbate is transported from the exterior to the interior

sites of the adsorbent particles, hence more time will then be consumed on diffusion of atrazine to binding sites. However, it remained constant after an equilibrium time of 120 min, which indicates that the adsorption had reached saturation. Therefore, the adsorption time was set at 120 min in each of the next experiments. Further increase in time after 120 min did not bring about any improvement. This is in agreement with the work done by Neera Singh [28].

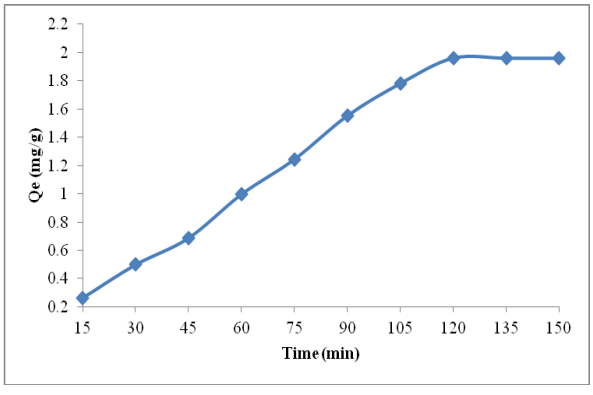

Figure 4:Effect of contact time on biosorption of atrazine

4.2.3. Effect of biosorbent dosage on biosorption of atrazine

Biomass dosage is an important parameter in adsorption studies as it gives the optimum dose at which maximum adsorption occurs. Figure 5 shows the effect of biomass dose on the adsorption of atrazine. The percentage adsorbed first increased with an increase in biosorbent dose due to increased surface area and more biosorption sites available for binding to atrazine [29]. Maximum removal was obtained at 0.9 g hence it was considered the optimum dose for adsorption experiments. After 0.9 g of biosorbent dosage there was no significant change in the amount of atrazine removed [30]. The trend is similar to work reported by Pathak and Dikshit [22]. They studied the effect of algae biomass dosage on the biosorption of atrazine.

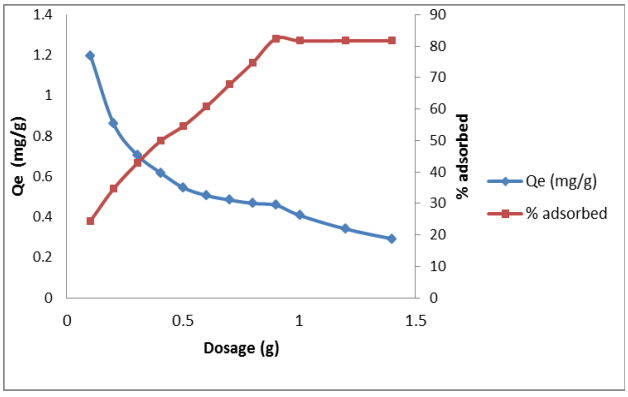

Figure 5:Effect of dosage on biosorption of atrazine

4.2.4. Effect of temperature on biosorption of atrazine

Temperature is a vital parameter in biosorption studies as it can have an effect on the rate of adsorption and amount absorbed. Figure 6 shows the effect of temperature on the adsorption of atrazine. From Figure 6, the amount of atrazine adsorbed increased from a temperature of 20°C to 25°C. At 25°C there was maximum atrazine adsorption. From 25 to 60°C the amount of atrazine adsorbed decreases with the increase in temperature suggesting the adsorption was exothermic in nature. Similar trends on the adsorption of pesticides onto various adsorbents were reported in literature [13,30].

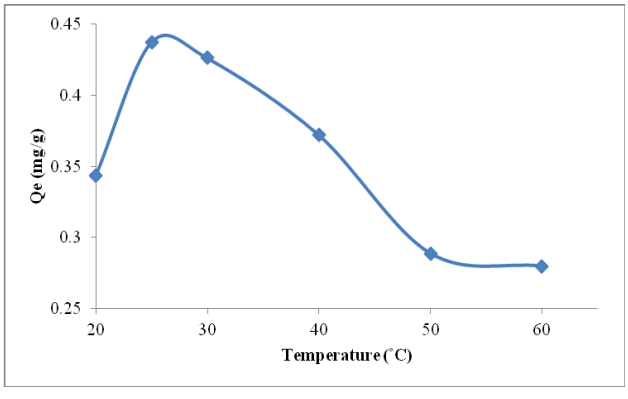

Figure 6: Effect of temperature on bisorption of atrazine

4.2.5. Effect of initial concentration on biosorption of atrazine

Figure 7 shows the effect of initial concentration on the adsorption of atrazine. At low concentrations, atrazine is adsorbed by specific active sites. At higher concentrations; lower adsorption is observed due to the saturation of adsorption sites. A decrease in percentage metal adsorption may be attributed to insufficient biomass surface area to accommodate all atrazine available in solution. There is an increase in the number of atrazine molecules competing for the available active sites on the surface [27].

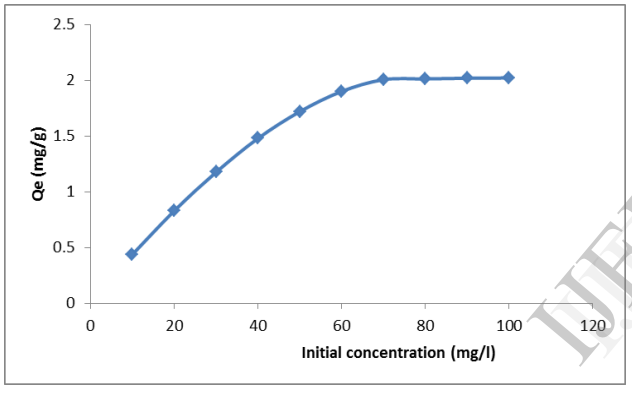

Figure 7: Effect of concentration on biosorption of atrazine

4.3. Equilibrium modeling (sorption isotherms)

Langmuir and Freundlich sorption isotherms were used to interpret the relationship between the amount of atrazine removed and its equilibrium concentration.

4.3.1. Langmuir adsorption isotherm

The Langmuir isotherm is mainly applied to monolayer adsorption. This is used to describe the sorption of solute from solution (Equation 3)

$$\frac{Q_e}{Q_m} = bC_e + \frac{C_e}{Q_e} \qquad (3)$$

Where; Q_e is the amount of atrazine adsorbed in mg/g, b is the Langmuir constant related to energy of sorption in L/mg, Q_m is maximum sorption capacity corresponding to complete monolayer coverage in mg/g, C_e is the equilibrium solute concentration in mg/L, R_L is the dimensionless equilibrium parameter in L mg^{-1} [31,32]. Figure 9 shows the graph of C_e/Q_e (g/L) against C_e (mg/L). Langmuir modeling describes adsorption on a homogeneous surface.

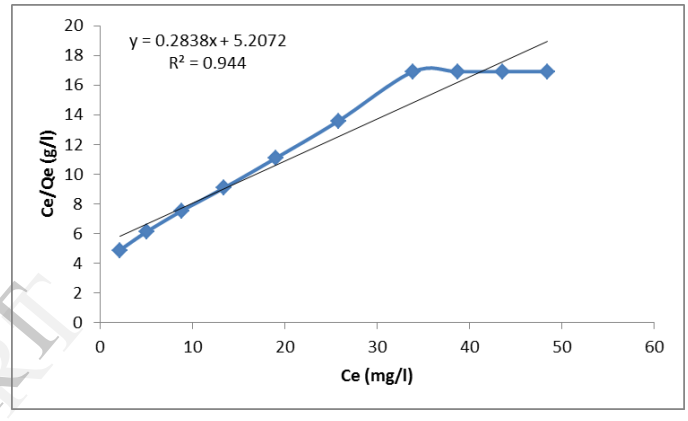

Figure 8: Langmuir isotherm for biosorptin of atrazine

The values of Langmuir constant Q_m and b are calculated from the slope and intercept of the linear plot C_e/Q_e versus C_e. In this research a biosorption capacity (Q_m) of 3.5236 mgg^{-1} was obtained. Itodo [24] investigated biosorption of atrazine using activated sheanut shells and the biosorption capacity was found to be -0.00772 mgg^{-1}.This shows that the bambara groundnut hulls are better biosorbents for the removal of atrazine. The use of zeolites as a biosorbent for atrazine has also been studied and the biosorption capacity was found to be 0.277 mgg^{-1} [33]. The bambara groundnut hull has a higher biosorption capacity and could be a reliable biosorbent for the removal of atrazine A lower value of b (0.0545) indicates a high affinity of the pesticide for the biomass. The essential feature of Langmuir isotherm model can be expressed by means of a separation factor of equilibrium parameter (RL). Values of RL indicate different types of biosorption isotherms namely: Linear (RL= 1); Favorable (0 <RL< 1); Unfavorable (RL> 1) and Irreversible (RL= 0). RL was found to be 0.6472

mg/L hence Langmuir biosorption isotherm is favourable. Correlation of determination R^2 was found to be 0.9440 for atrazine.

4.3.2. Freundlich adsorption isotherm

The Freundlich isotherm model describes adsorption on a heterogeneous surface and accounts for possible multilayer adsorption and nonlinear energy distribution for the adsorption sites [34]. The linearised form is represented by eaquation 4.

$$\ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \qquad (4)$$

Where K_f and 1/n are the Freundlich constants, related to adsorption capacity and adsorption intensity of the adsorbent respectively. The linearised Freundlich isotherm for the sorption of atrazine on bambara groundnut hulls is presented in Fig 9. The values of K_f (0.3221) and n (1.8096) were determined from plot of ln Q_e against ln C_e. These values show that Freundlich model could be a good model for the biosorption of atrazine. The value of R^2 (0.982) was regarded as the measure of the goodness of fit of experimental data on the isotherm model.

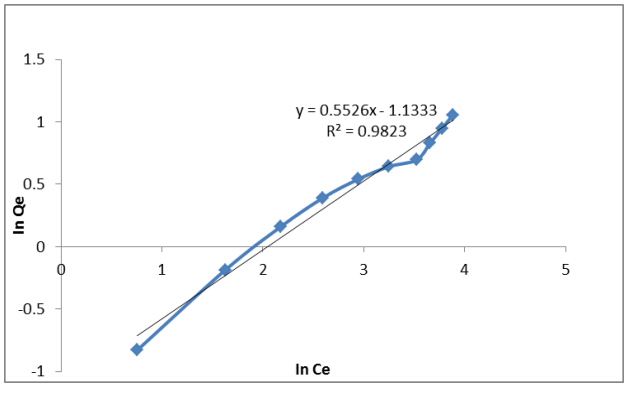

Figure:9 Freundlich isotherm for biosorptin of atrazine

The data fitted well into both isotherms. The isothermal biosorption parameters for the isotherms are shown in Table 4.1. The Langmuir and Freundlich isotherms compare well with those of other biosorbents that have been reported in literature [24,33]. The value of the parameters ($R^{2)}$ shows that bambara groundnut hulls are a good biosorbent for atrazine uptake from waste waters. Freundlich adsorption equation conforms better to the sorption results since the regression coefficient (R^2) value is higher (0.982) than that of the Langmuir equation (0.944). The value of Freundlich exponent in the range 1–10, indicates the favorable adsorption [34].

Table 1.Langmuir and Freundlich isotherm parameters

Isotherm type	Parameters	*Bambara groundnut hulls*
Langmuir	q_m	3.5236
	b	0.0545
	R_L	0.6472
	R^2	0.9440
Freundlich	k_f	0.3221
	n	1.8096
	R^2	0.982

4.4. Desorption studies of atrazine

Figure 10 shows the desorption studies performed on the bambara ground nut. The percentage desorption is higher when the amount of atrazine loaded on bambara groundnut hull is low. Poor desorption may be due to poor solubility of atrazine in solution or lower interaction between atrazine and the solvent. It may also be due to irreversible adsorption of atrazine on some adsorption sites [4]. The atrazine recovery efficiencies reported in literature ranged from 25 to 95% [18].

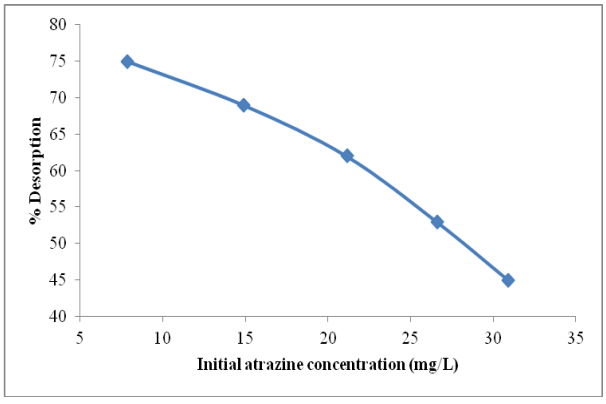

Figure 10: Desorption studies of atrazine

4.5. Kinetic studies

The rate constant for the adsorption of atrazine by bambara seed hulls was studied using the equation 5.

$$\log (Q_e - Q_t) = \log Q_e - k_1 \frac{t}{2.303} \qquad (5)$$

where Q_e is the amount of solute sorbed at equilibrium, Q_t the amount of solute sorbed at time t and k_1 the first order equilibrium rate constant. Figure 11 indicates that the adsorption process follows the first order rate expression. The first order equilibrium rate constant was found to be 0.01313 min^{-1}.

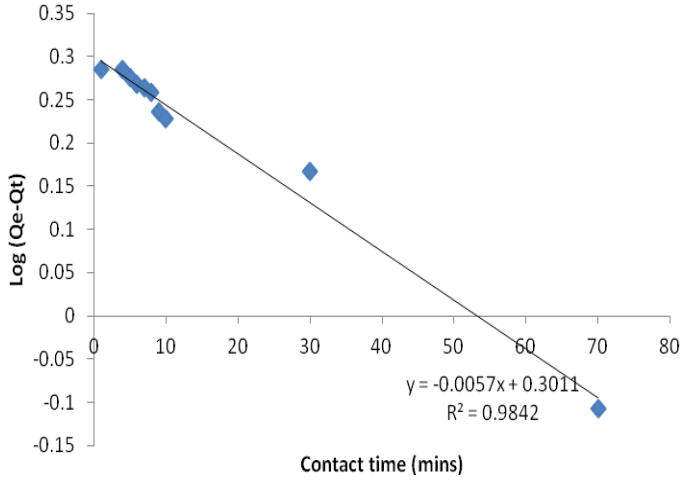

Figure 11: Pseudo first order plot for bambara groundnut hull biosorption

5. Conclusion

Low-cost agricultural waste of bambara groundnut hulls can be effectively used to remove atrazine pesticide from water. The sorption of atrazine onto bambara groundnut hulls is dependent on the initial atrazine concentration. Adsorption process was found to be highly pH dependent, with pH 7 being optimal and 0.9 g biomass was required at saturation point. Equilibrium experiments revealed that the dilute atrazine solutions reached equilibrium after 120 min. The results show that pH, biomass dose, initial concentration and contact time highly affect the overall atrazine uptake capacity of biosorbent. Hydroxyl and carbonyl groups were responsible for atrazine sorption. Recovery of less than 70% indicated that the functional groups present in the biosorbent are mainly responsible for chemical interaction between atrazine and biosorbent cell walls. The sorption isotherm studies demonstrate that the model which fits better is the Freundlich isotherm.

Acknowledgments

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