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International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.10, pp 552-566, 2017

Removal of atrazine from aqueous solution using untreated and sulphuric acid treated maize cobs biomass.

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Abstract : The increasing agricultural activities have led to discharge of herbicides in the environment. There is need to develop ways of removing herbicides from the environment as they pollute the environment. In this study the possibility of using untreated and sulphuric acid treated maize cobs to remove the herbicide atrazine from aqueous solution was investigated. The effect of initial concentration of atrazine, pH and temperature on adsorption was studied. The adsorption studies were conducted in the concentration range of 25ppm to 100ppm, pH range of 2 to 10 and temperature range of 30^{o}C to 80^{o}C. The results obtained indicate that pH value of 5andtemperature of 30^{o}C cause optimum adsorption of atrazine. The experimental data fitted well the Langmuir adsorption isotherm. Fourier Transform Infrared spectroscopywas used to identify the functional groups on the surface of the adsorbents. Functional groups typical of lignocellulosic materials were observed. Surface morphology was studied using scanning electron microscopy. The results obtained suggest that sulphuric acid treatment changed the surface of the adsorbent by increasing the number of pores. The maximum adsorption capacity was 99.8% for acid treated maize cobs and 99.4% for untreated maize cobs. Thermodynamic parameters, ΔG^{o}, ΔH^{o} and ΔS^{o} were determined and their values suggest the atrazine adsorption is spontaneous and endothermic. The results of this present study suggest that sulphuric acid treated maize cobs biomass and untreated maize cobs biomass can be used as efficient low cost biosorbents for the adsorption of atrazine from aqueous solution.

Keywords : Atrazine adsorption, acid treated biosorbents, adsorption isotherms.

1.0 Introduction

Recently there has been an increase in agricultural activities due to increasing demand for food as populations are growing. This has led to the use of herbicides to ensure high yields are obtained. Leaching of herbicides applied to agricultural land is one of the main reasons for organic pollution in several streams[1]. Herbicides are harmful to life because of their toxicity, carcinogenicity and mutagenicity thus there is need to develop ways of removing them from the environment.

Activated carbon has been successfully used to remove toxic organic pollutants from water but its price is high for large scale treatment and regeneration of activated carbon is also difficult[2].Commercial activated carbon is considered to be expensive due to the fact that it is from a non-renewablere source[3].Efficient techniques for the removal of organic compounds from water include coagulation, filtration with coagulation, precipitation, ozonation, ion exchange, reverse osmosis and advanced oxidation processes[4]. However the use of such methods is limited because of high capital cost and operational costs. Biosorption is currently being used extensively for the removal of organic contaminants in waste water treatment[5]. Natural materials especially those from agricultural origin are now of interest as biosorbents due to their low cost and availability[6]. They also do not present any disposal problem[7]. Thus biosorption is an environmentally friendly method to remove organic pollutants such as herbcides. Activated carbon from agricultural waste has the advantage of high adsorption capacity for organic pollutants such as herbicides due to their high surface area micro-porous structure and non-polar character[8]. Atrazine is one of the most widely used herbicides in the USA, Australia, Mexico, Zimbabwe, Brazil and China[9]. Numerous studies have been done on the use of agricultural waste products such as green coconut shells, rice husks, bamboo wood, pinewood, cork waste etc., to remove organic pollutants from aqueous solution[10, 11]. After harvesting of maize, the maize cobs are just thrown away. In Zimbabwe maize cobs can be used to make fire but because they generate a lot of smoke, they are rarely used. The use of maize cob waste as precursor for activated carbon manufacture could provide an attractive route for its disposal[12]. Yang reported the use of nylon 6 to adsorb atrazine from waste water[13].Lupul and other researchers investigated adsorption of atrazine from water using hemp stem activated carbon[3]. Oxidised multi walled carbon nanotubes were also used to adsorb atrazine from aqueous solutions[12]. No studies have been reported on the use of maize cobs to remove atrazine. Most of the studied adsorbents are not readily available thus there is need to develop a low cost adsorbent that is readily available for developing countries. Chemical treatment has been reported to alter the functional groups of the surface of lignocellulosic materials and that has an effect their adsorbent properties[14]. This research seeks to use untreated and acid treated maize cobs for the biosorption of atrazine from aqueous solution.

Figure 1: Photo of maize cobs

2.0 Materials and Method

2.1 Preparation of maize cobs

The maize cobs were collected from a farm in Mazowe district, Zimbabwe. The cobs were first washed with tap water to remove sand and then rinsed with distilled water. They were spread out on empty polythene sacks and left to dry in the sun for several days. The dry maize cobs were first pounded in a pestle and mortar then ground using a blender. The resulting substance was sieved and particle sizes in the range 250-300µm were collected. The resulting powder was divided into two portions A and B. Portion A was bottled as it is and it constituted untreated maize cobs (UMC). 200g of portion B was then acid treated as outlined below.

2.2 Preparation of acid treated maize cobs

200g of the maize cob powder from portion B was carefully added to 200ml of 98% sulphuric acid in a beaker inside a fume hood. The mixture was left in the fume hood until completely digested. The resulting solid was repeatedly washed with deionised distilled water. It was then soaked in 5% $NaHCO_3$ to neutralise unreacted acid and this was then followed by washing with hot distilled water. The sample was again washed with distilled deionised water until a pH 7 was achieved. The sample was then dried in an oven at 100^oC overnight and kept in a closed reagent bottle. The resulting maize cob was then labelled ATMC (acid treated maize cobs).

2.3 Characterization of untreated and acid treated maize cobs

2.3.1 Determination of moisture content

Samples of untreated and acid treated maize cobs were first weighed (1.5 g) and heated in an oven at 100^oC to dry them until they had constant mass. During heating the samples were weighed at 30 minute intervals until constant mass was obtained for three consecutive readings. The difference in mass between the initial and constant mass represented the moisture content in each sample.

2.3.2 Determination of organic matter content

The two samples obtained from the determination of moisture content were weighed then placed in a muffle furnace at a temperature of 600^oC and heated for 2hrs. The residual product was weighed for each sample. The difference in mass between initial and final mass represented the organic matter content of both samples of maize cobs.

2.3.3 FTIR analysis of samples

FT-IR spectra of untreated and acid treated maize cob biomass were recorded in ATR mode within the 400- 4000 cm^{-1} wave number range at 4 cm^{-1} resolution. 50 scans were run for each sample and averaged using a FTIR(Thermo Fisher Scientific, Niolet iS5, UK). Fig. 2shows the FT-IR spectra obtained.

2.3.4 Scanning electron microscopy

TheSEM micrographs were obtained using aX-650, (Hitach, Japan). The samples were placed onto the sample holder using a double sided tape in such a way that they were presented to the analysing beam. Figs. 3-4 show the typical SEM micrographs obtained.

2.4 Adsorption studies

The stock solution of atrazine(1000ppm) was prepared by adding $67.3cm^3$ of atrazine to a 1:1 mixture of methanol and deionised distilled water in 1L volumetric flask. Distilled deionised water was then added to the mark. Test solutions were prepared by diluting the stock solution to desired concentrations. Biosorption of atrazine was performed by agitating $250cm^3$erlenmeyer flasks on mechanical shaker at 100rpm. The flasks contained the standard atrazine solution and known amounts of both acid treated and untreated maize cobs. An equilibrium time of 2hrswas allowed after preliminary work had shown that adsorption was nearly complete in one hour. After equilibration, the samples were centrifuged to settle the fine particles and the supernatant solutions were poured into beakers. The final concentration of atrazine in each flask was determined using a UV-Vis spectrophotometer (ThermoFisher Scientific Genesys 10S).Four replicates were used with each case.

2.4.1 Effect of initial concentration of atrazine

Effect of initial concentrations on adsorption of atrazine by UMC and ATMC was investigated in the range 25ppm to 100ppm at room temperature, contact time of 2hrs, a constant pH of 5 and biosorbents dosage of 1g. The flasks were shaken on a shaker for two hours after which the residual concentration of atrazine in each flask was determined using a UV-VIS spectrophotometer.

2.4.2 Effect of pH

Five Erlenmeyer flasks were set up with 1g of AMTC in each and 100ml atrazine solution at room temperature. The pH in each flask was determined using a pH meter and it was adjusted by adding either 0.1M H_2SO_4 or 0.1M NaOH until the desired pH was obtained. The initial concentration of atrazine in each flask was 100ppm.Another set of five Erlenmeyer flasks were set up with similar contents with UMC as biosorbent. The flasks were agitated on a shaker at the same time for 2 hrs after which the concentration of atrazine remaining in each flask was determined by a UV- VIS spectrophotometer. .Again four replicate measurements were done at a pH range of 2 to 10.

2.4.3 Effect of temperature

Different temperatures ranging from 30^oC to 80^oC were used with a constant pH of 5, initial concentration of atrazine of 100ppm and biosorbent dosage of 1g and contact time 2hrs to study the effect of temperature. The procedure was repeated for both ATMC and UMC. The flasks were shaken in a temperature controlled water bath at the required temperature. The residual concentration of atrazine in each flask was determined by a UV- VIS spectrophotometer.

2.5 UV-VIS analysis

The concentration of atrazine solution before and after biosorption was determined using UV-VIS spectrophotometer (Thermo Fisher Scientific Genesys 10S). The absorbance of atrazine was read at a wavelength of 320nm [1].

3.0 Results and Discussion

3.1 Characterisation of adsorbents

3.1.2 Moisture and organic matter content

The UMC had a higher water content of 8.5 ± 0.1% per 100g of adsorbent compared to 6.0 ± 0.2% per 100g of ATMC adsorbent and organic matter content of 7.0 ± 0.1% per 100g of UMC compared to 9.6 ±0.3% per 100g of ATMC adsorbent. ATMC showed a higher organic matter content and low water content,this enhances the adsorption capacity of ATMC. Most of the water content had been removed by the treatment with acid.

3.1.3 FT-IR spectra of UMC and ATMC before after adsorption of atrazine

FT-IR spectroscopy was used to analyse the functional groups of the maize cobs. Figure 2 shows FTIR spectra of treated and untreated maize cobs biomass. The FTIR bands for the adsorbents are summarized in table 1.

Table 1: FTIR results

Type of Maize Cob	Bands (cm^{-1})	Assignment	Reference
UMC	3334	O-H	15
	2918	C-H	16
	1632	C=C	17
UMC adsorbed with ATR	3330	O-H	18
	1719	C=O	19
	1032	C-O or C-H with conjugated aromatic ring)	20

ATMC	3381	O-H	17
	1588	C=C	18
	1017	C-O or C-H	19
ATMC adsorbed with ATR	1577	C=C	15
	1158	C-O or C-H	20
	1374	Aromatic C-H	18

The FTIR spectra of both UMC and ATMC show the presence of O-H bonds (Figure 2, Table 1). It can be suggested that the adsorption of ATR occurs through the interaction between the tertiary amines of the atrazine and the O-H bonds of the maize cob[8]. In the ATR ring the para N is a site where ATR accepts an H-bond whereas the ethylamine side chain can be an H-bond donor[2]. In another research carried out by Chingombe et al. they found that ATR was able to form H-bonds with $^{-}$COOH and phenolic groups[21]. The ATMC had more O_2 groups shown by the presence of C-O bonds after acid digestion. Thus concentration of O_2 functional groups on the carbon surface of the activated carbon can be enhanced through acid treatment. Wet oxidation using different oxidants like H_2O_2, H_2SO_4, and HNO_3 is the common approach used to incorporate O_2 groups[3]. From this it can be suggested that the adsorption of ATR occurs through acid-base interactions between the basic atrazine and the acidic carbon surface.

The most prominent peak change between UMC and ATMC occurred around 1747cm^{-1}.This peak for ATMC became much sharper than that of UMC which may be caused by a large amount of C=O groups which appeared after acid treatment. Comparing the FTIR spectra of ATMC and ATMC adsorbed with ATR, after adsorption new peaks emerged at around 881cm^{-1} and 1394cm^{-1}, suggesting that the atrazine molecules were bound to different extents by the ATMC and the UMC. The atrazine molecules were closely and strongly bound to the ATMC than to UMC. Peak heights also changed from 1740cm^{-1} to 1056cm^{-1} and 2924cm^{-1} suggesting that a large number of ATR molecules were attached on the surface of both UMC and ATMC.

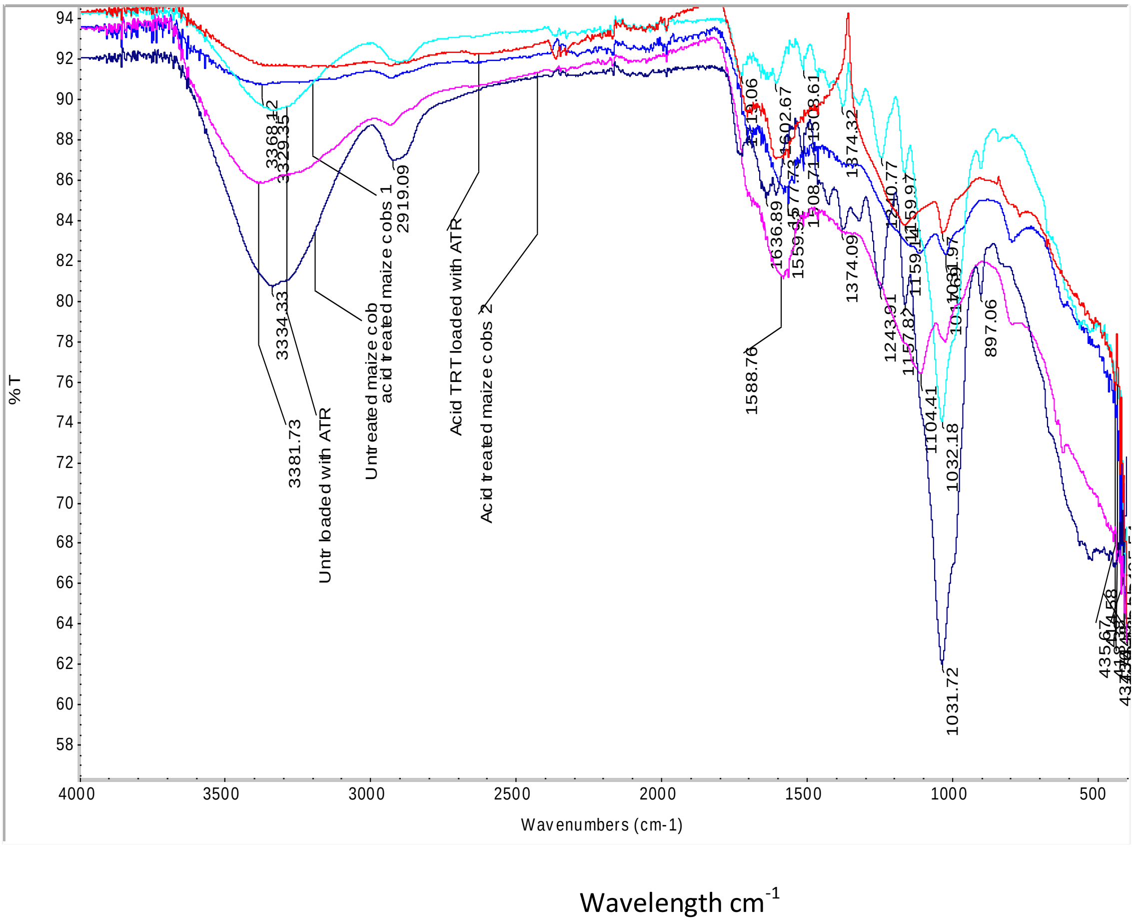


Figure 2: FT-IR spectra of UMC and ATMC before and after adsorption of atrazine

3.1.4 Scanning electron microscopy

A rougher surface with regular tunnel like structures is revealed for the untreated maize cob adsorbent (Figure 3a). In addition to this many small pores are observed on the surface of the tunnel like structures. Rough features improve the molecular adsorption of species. A more compact morphology is revealed for the untreated maize cob adsorbent. The SEM micrographs of both adsorbents consist of fibres with significant pores and uneven structure (Figure 3.-4). These surface characteristics substantiate higher adsorption capacity observed. The micrographs also reveal abundant cavities within the adsorbents. These cavities increase the surface area of the adsorbents. Micrograph of acid treated maize cobs (Figure 4) shows a lot of cavities and pores but the tunnel like structure disappeared most likely due to the crushing procedure. The cavities may be due to the removal of extractives; hemicelluloses and lignin. Acid treatment results in the breakdown of the lignocellulosic material. After adsorption the surface morphology changed considerably (Figure 3b and 4b). The small penetrable pores were covered and merely left some faint outline of the pores. This might be due to the attached atrazine molecules on the surface of the adsorbent.

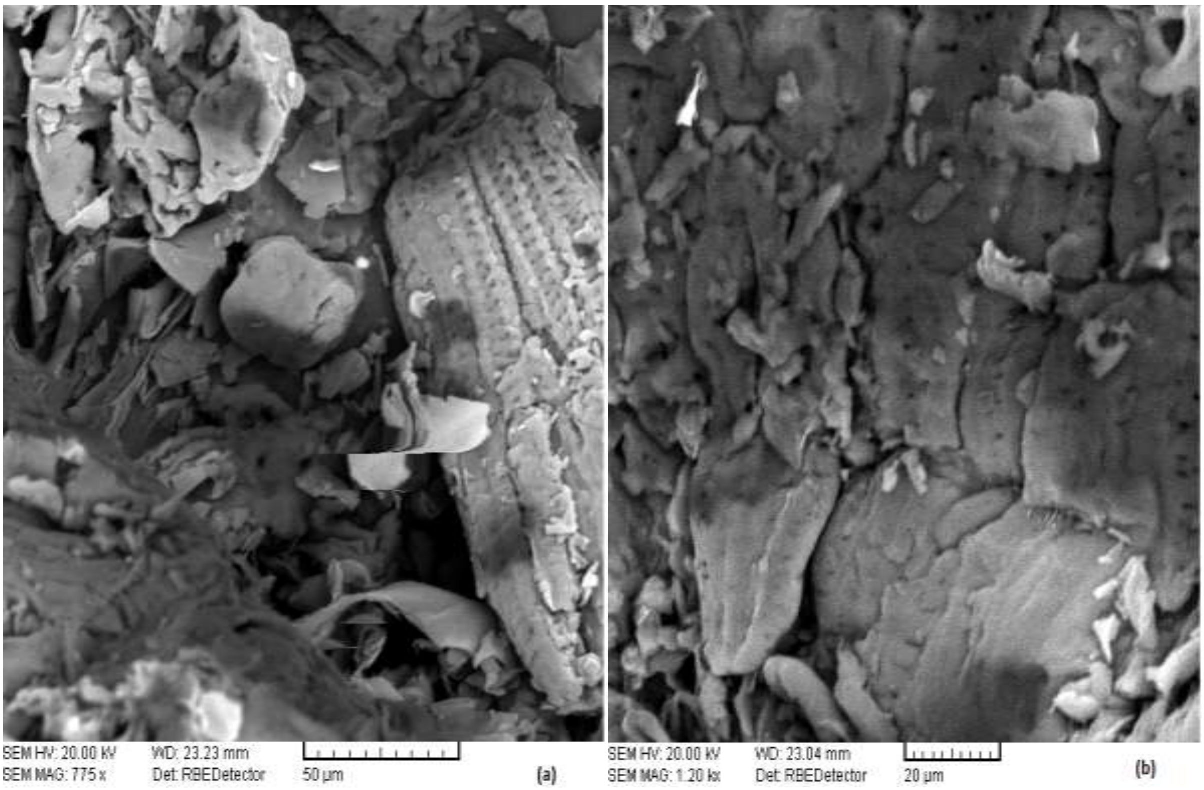


Figure 3: SEM micrographs of (a) untreated maize cobs and (b) untreated maize cobs adsorbed with atrazine.

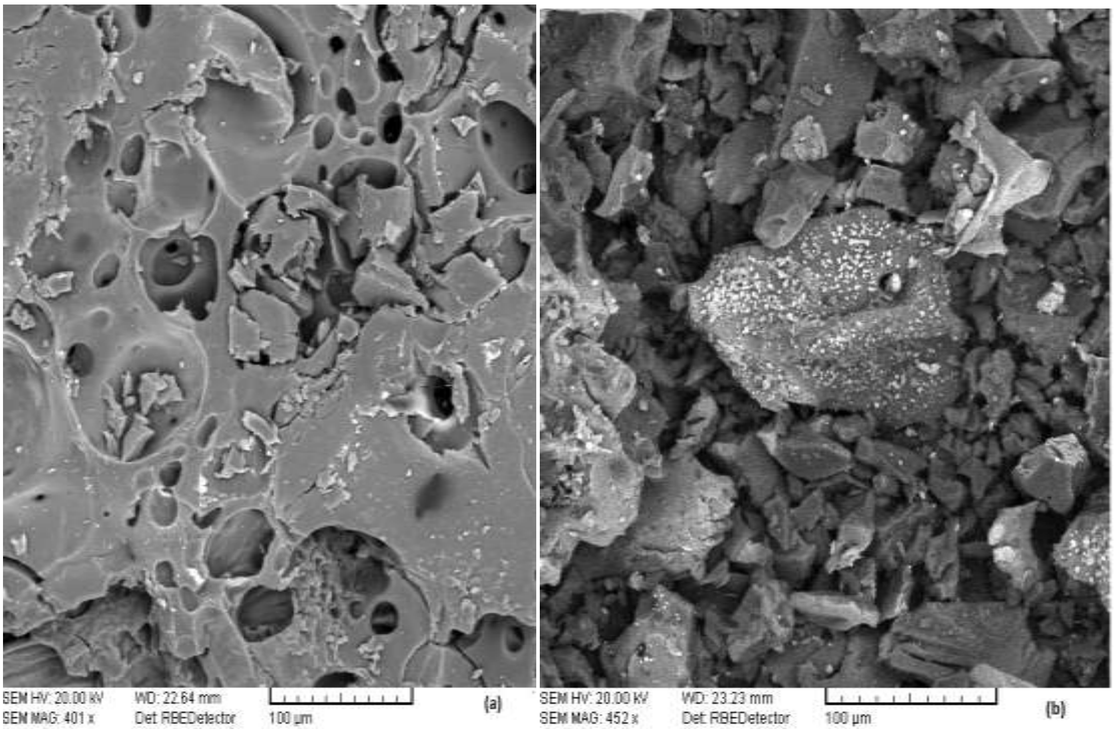


Figure 4: SEM micrographs of (a) acid treated maize cobs only and (b) acid treated maize cobs adsorbed with atrazine.

3.2 Factors that affect atrazine adsorption

3.2.1 Effect of Initial Concentration of Atrazine

Equation 1 was used to calculate the amount of adsorbate at equilibrium.

$$Q_e = \frac{(C_o - C_e)}{m} \qquad (1)$$

Where Q_e is the equilibrium amount of adsorbate, C_o is the initial concentration of the adsorbate C_e is the equilibrium concentration of adsorbate. V is volume used and m is the mass of the adsorbent.

The initial atrazine concentration provided the driving force to overcome mass transfer resistance of the herbicide between the aqueous and solid phases[3].The percentage removal of atrazine decreased with increase in the initial concentration of ATR (Figure 5a). The maximum adsorption capacity of 99.3% was obtained with an initial concentration of 50ppm for ATMC while for UMC, it was 96.7% obtained with an initial concentration of 25 ppm. For ATMC, the rate of external diffusion accelerated with increase in the initial concentration resulting in more atrazine adsorbing on the surface of the ATMC[22]. Under different initial atrazine concentrations, the q_e values for both UMC and ATMC changed. As the initial concentration of atrazine increases from 25ppm to 100ppm, the q_e values decrease. At higher initial concentration the ratio of atrazine molecules against the available adsorption sites became higher. As a result fewer atrazine molecules were adsorbed [23].

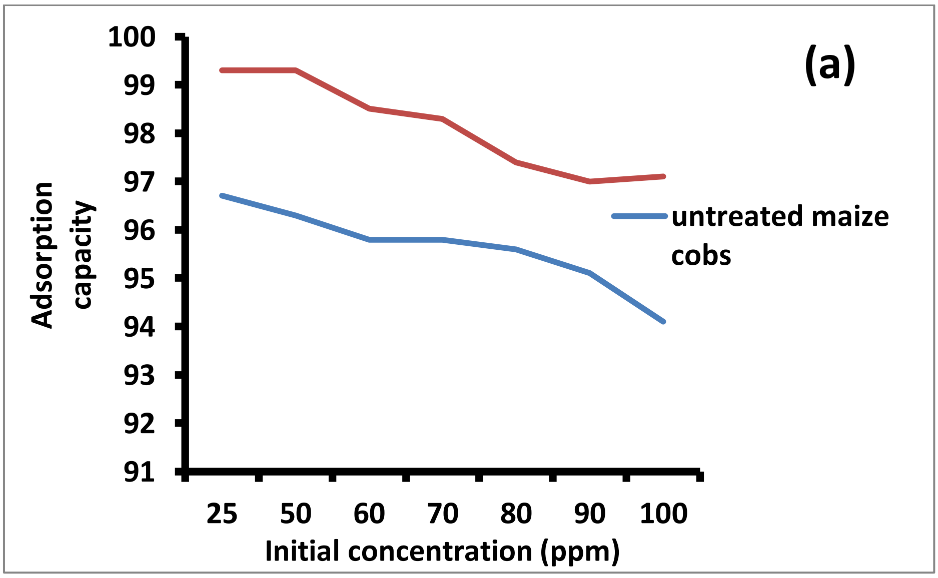
When the initial concentration increased above 50ppm the adsorption sites were close to saturation and adsorption decreases.Additionally at higher initial concentration the ATR molecules have to penetrate the boundary layer after the rapid attachment on the outer surface of biosorbents.At lower initial concentration the adsorption mainly occurred rapidly on the outer surface of biosorbents because there will be many available sites.The results also suggest that ATMC is a slightly better adsorbent than UMC i.e. under the same conditions the former achieved a maximum adsorption capacity of 99.3% and the latter achieved 96.6%.

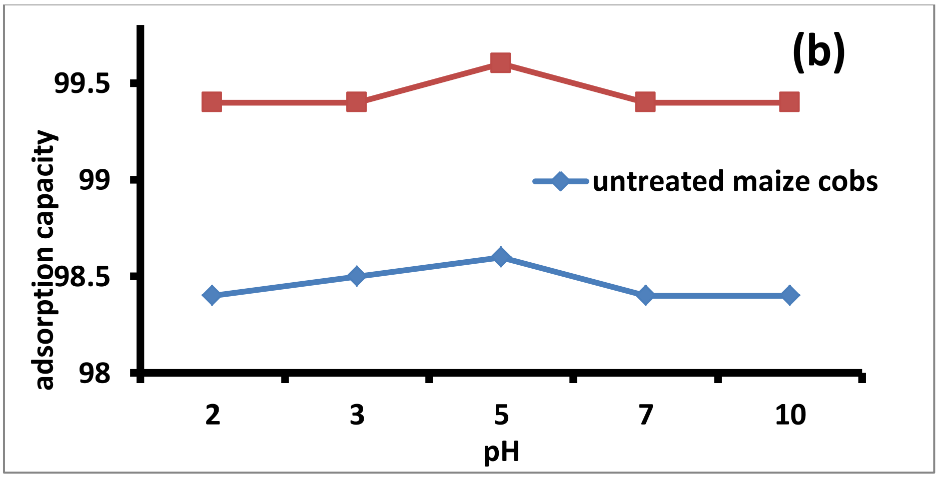
3.2.2 Effect of pH.

Figure 5b shows that adsorption capacity rose steadily up to pH 5 beyond which it began to decrease for both UMC and ATMC. ATR is adsorbed on the carbon surface as uncharged species. The pH range of 2-10 used in the study caused both the ATR and adsorbents to be protonated and deprotonated to produce the different surface charges. A decrease in pH enhanced ATR adsorption because ATR is weakly basic with pKa of 12.3 so it can interact with the acidic adsorbents. The functional groups of both UMC and ATMC are anionic and they release negative charges when dissolved in water[21]. It seems that the positively charged species of the ATR can cause the destabilization of the negatively charged molecules by adsorbing onto them[21]. The pH of solution hasan effect on the surface charge of the adsorbent and the degree of ionization of the adsorbate. Under acid conditions, atrazine become positively charged due to protonation leading to stronger electrostatic attractive interactions with the negatively charged anionic groups on the adsorbent surface. However, the degree of ATR protonation may decrease with increase in pH, which can weaken the electrostatic attraction resulting in the observed decrease in the adsorption capacity[21].

3.2.3 Effect of temperature

At 30 °C adsorption capacity was 99, 6 % for ATMC and 99, 4 % for UMC (Figure 5).As the temperature increased above 30°C, the adsorption capacity increased. From these results it can be suggested that the amount of adsorption is inversely proportional to the temperature although there is no significant decrease in the adsorption capacity. The results also suggest lower adsorption capacity for UMC than ATMC as shown in figure 5.





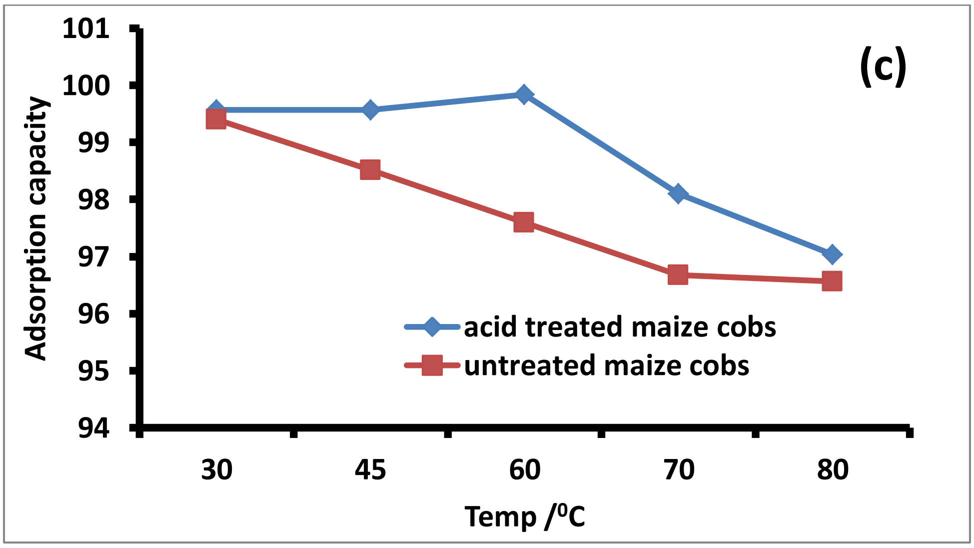


Figure 5: Plot of effect of(a) initial concentrationof atrazine (b) pH, (c) temperature versus adsorption capacity for UMC and ATMC.

3.3 Adsorption isotherms

3.3.1 Freundlich Adsorption Isotherm

Freundlich gave an empirical expression representing the isothermal variation in 1909 which is today known as Freundlich adsorption isotherm[24]. This model takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. It can be applied to the multilayer adsorption with non uniform distribution of adsorption heat and affinities over the heterogeneous surface[12]. Freundlich isotherm is expressed as in equation 2.

$$Q_e = KfC_e^{1/n} \quad (2)$$

Where Q_e is equilibrium concentration, K_f is approximate indicator of adsorption capacity, C_e is equilibrium concentration of adsorbate and $\frac{1}{n}$ is approximate indicator of adsorption intensity. When is $\frac{1}{n}$ less than 1 there is high sorption [12].

3.3.2 Langmuir Isotherm

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneity adsorption energy. It is based on the following assumptions[13]: The surface of the adsorbent is uniform i.e. all the adsorption sites are equal, there is no interaction between adsorbed molecules, all adsorption occurs through the same mechanism and the adsorbed layer is made up of a single layer of molecules[24]. The Langmuir isotherm equation is derived from rational consideration and is given by equation 3;

$$q_e(1+bC_e) = qmbC_e \quad (3)$$

Where q_e is amount of solute adsorbed per unit weight of adsorbent at equilibrium mgg^{-1}, C_e is equilibrium concentration of the solute in the bulk solutions, qm is maximum adsorption capacity mgg^{-1} and b is a temperature dependent constant Lmg^{-1}.The adsorption data for atrazine adsorption was fitted in the Langmuir and Freundlich isotherms for all the investigated parameters using equation 2 and 3(Figure 6 to 11).The data was described well with Langmuir thanFreundlich adsorption isotherm as shown by the correlation coefficient values (Table 2). Langmuir adsorption was also reported for atrazine adsorption onto activated carbon prepared from rubber tire waste[2]and commercialactivated carbon fibers[25]. Some researchers have reported that atrazine adsorption fits best on the Freundlich isotherm[3]. In the present study all equilibrium concentrations corresponds to L-type isotherms according to Giles classification as all their slopes are less than 1.

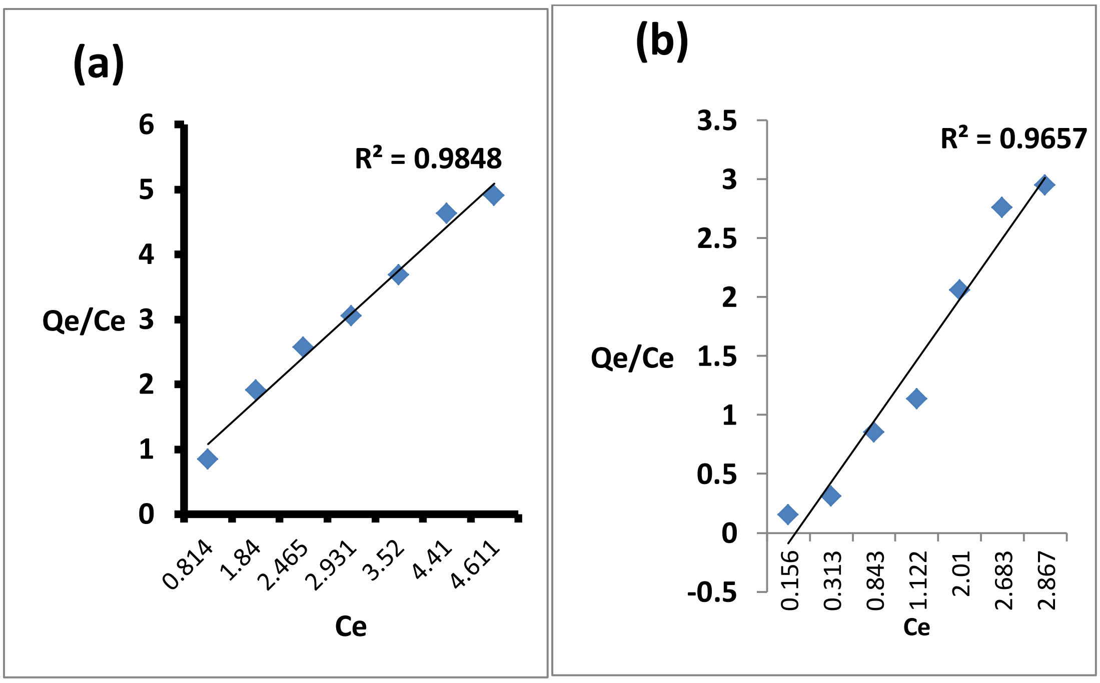


Figure 6: Langmuir adsorption isotherm for (a) UMC and (b) ATMC) for the effect of initial concentration.

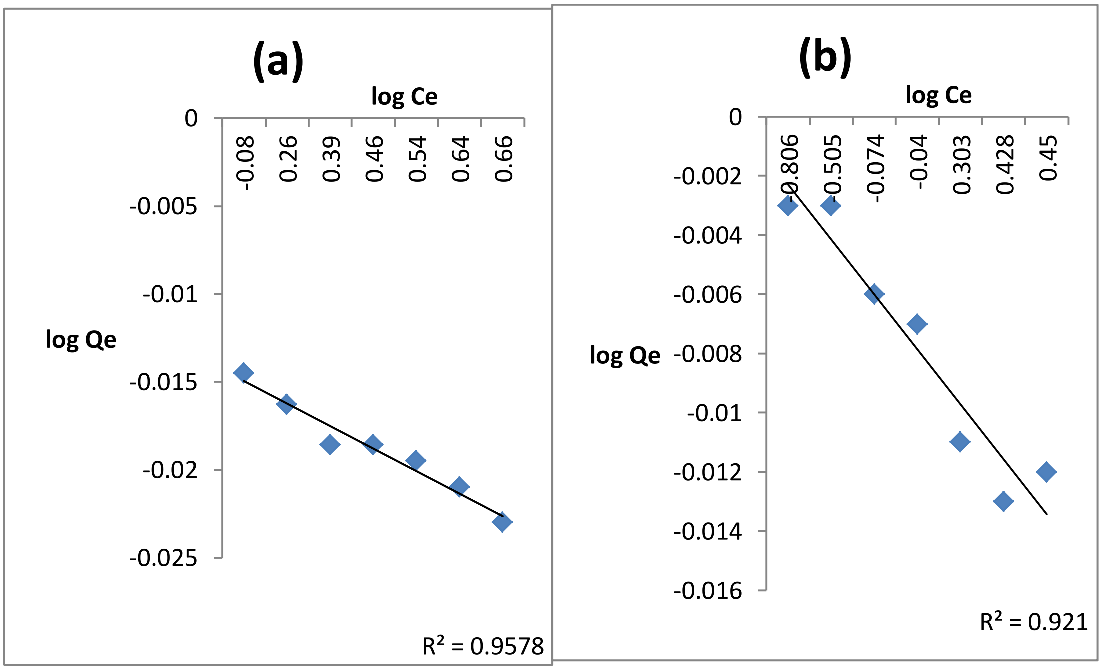


Figure 7:Freundlich adsorption isotherm for a) UMCand b)ATMC for the effect of initial concentration.

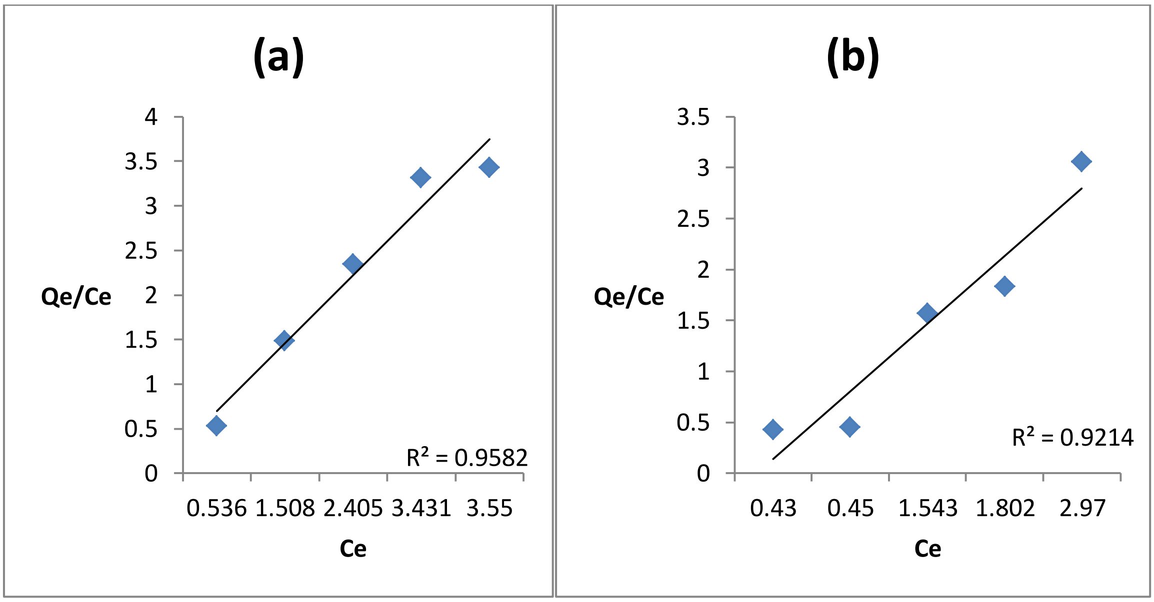


Figure 8: Langmuir adsorption isotherm for a) UMC and b) ATMCfor the effect of temperature

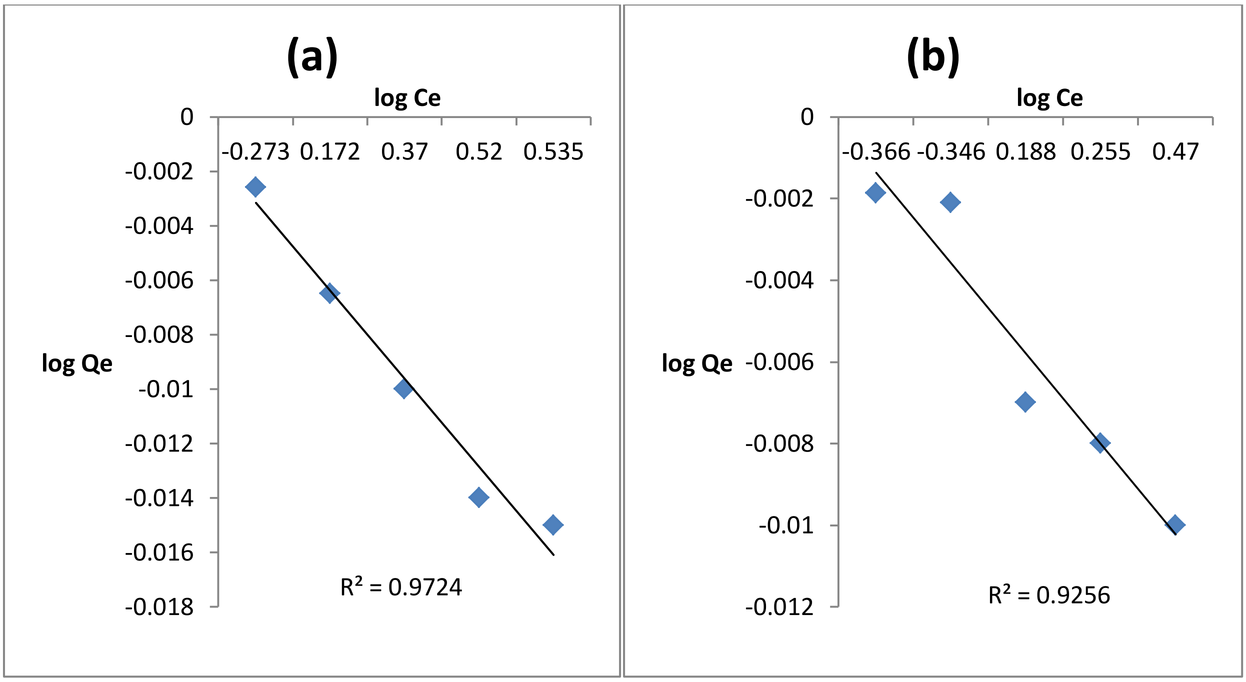


Figure 9: Freundlich adsorption isotherm for a) UMCand b) ATMC for the effect of temperature

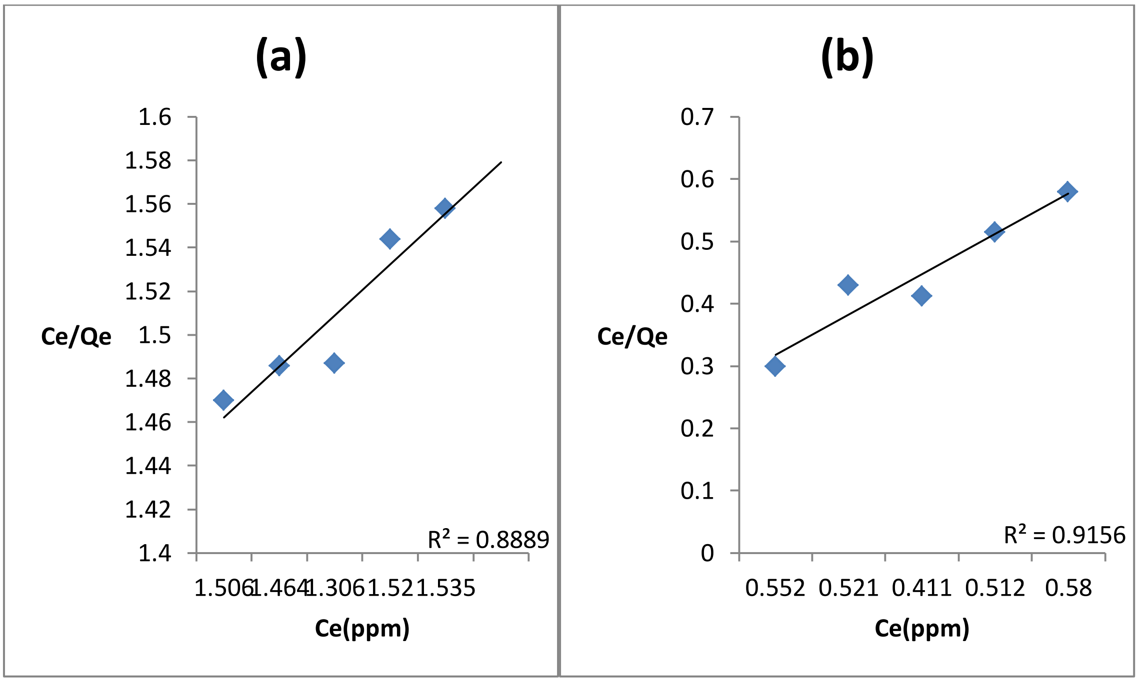


Figure 10: Langmuir adsorption isotherm for a) UMC and b) ATMCfor the effect of pH

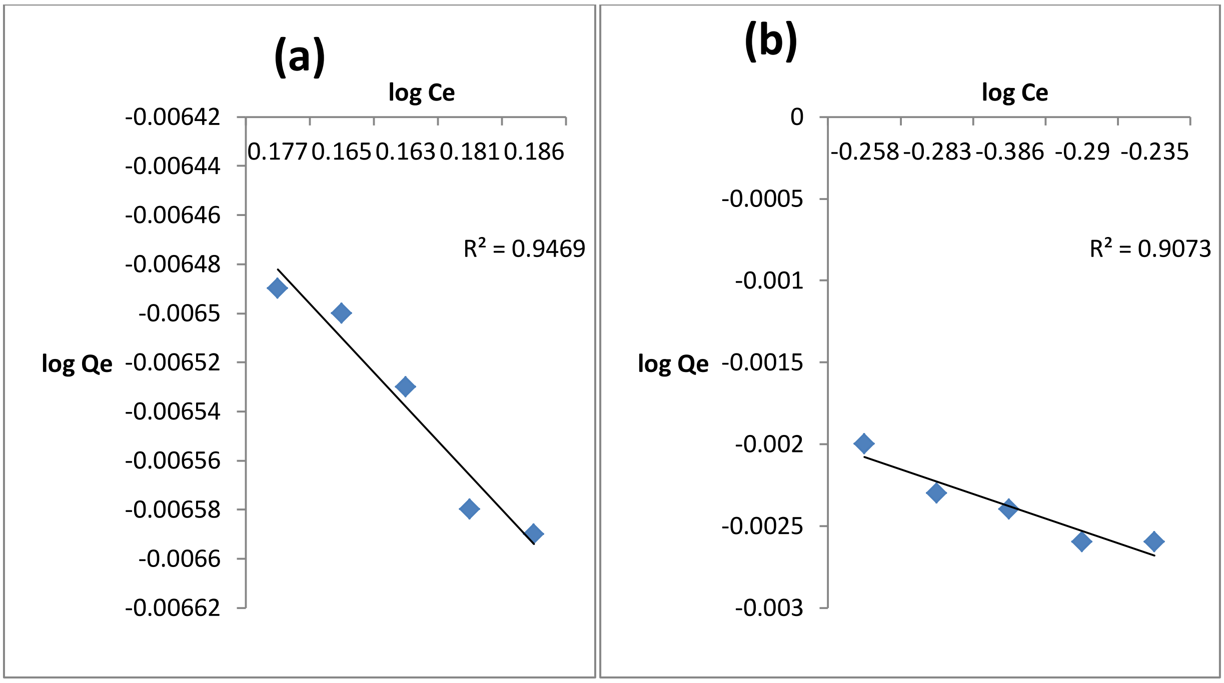


Figure 11: Freundlich adsorption isotherm for a) UMC and b) ATMC for the effect of pH.

Table 2: Langmuir and Feundlichparameters for atrazine adsorption on UMC and ATMC

Adsorbent		Langmuir Parameters			Freundlich Parameters		
		R^2	b	Q^o	R^2	K_f	1/n
UMC	initial concentration	0.98	1.64	1.50	0.92	0.97	-0.001
	temperature	0.95	-11.67	1.31	0.92	1.0	-0.003
	pH	0.88	0.02	42.74	0.94	0.99	-3E-05
ATMC	initial concentration	0.96	-0.86	1.93	0.95	0.99	-0.002
	temperature	0.94	-1,27	1.51	0.92	1.00	-0.0022
	pH	0.91	0.25	15.50	0.90	0.99	-0.001

3.4 Thermodynamic parameters for adsorption of atrazine

The equilibrium constant K_C at different temperatures was calculated for both UMC and ATMC using equation 4.

$$K_C = \frac{C_a}{C_e} \tag{4}$$

Where C_a is the amount of atrazine adsorbed mgl^{-1} per weight mass of adsorbent and C_e is the equilibrium adsorbate concentration in aqueous phase. ΔS^o and ΔH^o for the process was determined from the plot of $\ln K_c$ against $\frac{I}{T}$ (Figure 12) where ΔH^o is the slope and ΔS° is the intercept derived from the following relationship shown in equation 5.

$$InK_c = -\frac{\Delta G^o}{RT} = \frac{\Delta H^o}{RT} + \frac{\Delta S^o}{R} \tag{5}$$

Where R is ideal gas constant, T is Temperature. The Gibbs free energy ΔG^o was determined at different temperatures using equation 6.

$$\Delta G = -RTInK_c \tag{6}$$

The ΔH values for both UMC and ATMC are positive suggesting that the adsorption process is endothermic (Table 3). The negative Gibbs free energy values suggest that ATR adsorption by maize cobs biomass is a spontaneous process. The variation of energy for physical adsorption is usually substantially smaller than that of chemisorptions because physical adsorption is non- specific. On the contrary chemical adsorption is similar to ordinary chemical reactions in that it is highly specific[23]. If the values of ΔH^o are lower than 40 kJmol^{-1} and the values of ΔG^o are within the range of -20 and 0 kJmol^{-1} physical adsorption is the dominant mechanism [15]. The values obtained in this study (Table 3) are within the range for physical adsorption thus physical adsorption was dominant for ATR adsorption by maize cobs biomass.

Table 3: The thermodynamic parameters for the adsorption of atrazine using acid treated and untreated maize cobs.

Adsorbent	ΔH^o (KJmol^{-1})	ΔS^o(KJmol^{-1})	ΔG^o(KJmol^{-1})
UMC	+0.452	-5.350	-13.040
ATMC	+0.446	-5.929	-18.790

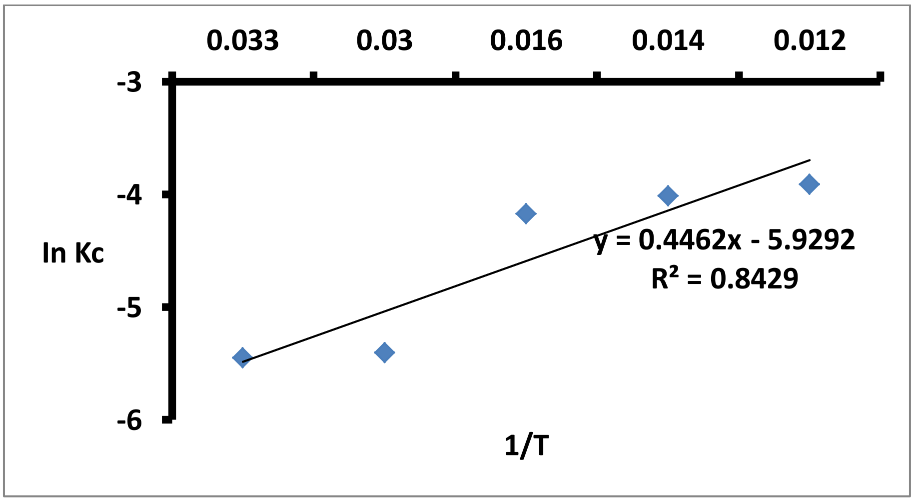


Figure 12:The adsorption thermodynamics for acid treated maize cobs.

Conclusion

The study showed that both UMC and ATMC can be used for effective removal of ATR from aqueous solution although ATMC has a higher adsorption capacity than UMC. The removal of ATR was shown to be dependent on pH and maximum removal was obtained with pH 5. Further Increase in temperature resulted in decrease in the adsorption process for both UMC and ATMC. Data obtained fitted well with the Langmuir adsorption isotherm confirming monolayer adsorption mechanism. The negative Gibbs free energy, ΔG^o values shows that the adsorption of atrazine by UMC and ATMC is spontaneous. The positiveenthalpy of adsorption (ΔH^o) values found indicates that the adsorption process is endothermic. This investigation hasdemonstrated that both untreated and sulphuric acid treated maize cobs are efficient and low cost biosorbents for the eco-friendly removal of atrazine from aqueous solutions.

Conflict of interest

The authors declare no conflict of interest.

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