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Article

Preparation, Characterization and Application of Rice Husk Adsorbent in the Removal of Ampicillin from Aqueous Solution

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Abstract: In this study, the adsorption of ampicillin was carried out using the batch adsorption studies. An adsorbent was extracted from rice husk using a sol-gel method with 1.0 M HCl. The physicochemical properties such as moisture content, attrition, bulk density and porosity were found to be 7.25%, 57.60%, 1.34 g/m^3 and 0.65 respectively. Batch adsorption experiments of the adsorbent were conducted under various conditions such as temperature, pH, adsorbent dosage, concentration of the adsorbate and contact time using a standard solution of ampicillin. Percentage removal of ampicillin increase from 30-45 ºC and decreases after 45 ºC with optimum operating temperature of 45 ºC, Percentage removal of ampicillin decrease at different pH varying from 3-5 and 9-11, the increases in pH was from 5-9 with 9 been the highest pH of adsorption. The variation of contact time showed a decrease from 10-30 minutes. Percentage removal of ampicillin showed a sharp decrease as adsorbent dosage increase from 0.4-0.6 g. The increase in percentage removal of the adsorbate at various concentrations was inconsistent. The experimental data were tested using adsorption isotherms of Langmuir, Freundlich and Tempkin. The R^2 value of Langmuir, Freundlich and Tempkin was found to be 0.811, 0.705 and 0.639. Langmuir model was found to be the best fit for the data.

Keywords: adsorbent; adsorption; Ampicillin; Rice Husk.

1. Introduction

The concerns about environmental contaminants has widened to include not just persistent organic pollutants (POPs) but also pharmaceuticals[1]. Pharmaceuticals are chemical substances such as Antipyretics, antimalarials, analgesics, antibiotics, mood stabilizers, hormone replacements, oral contraceptives, tranquilizers and statins that are used in the treatment of diseases due to their biological activity[2]. The presence of pharmaceuticals in the environment has sparked serious concerns over the past decade due to the harmful effect some pharmaceuticals pose to life. Pharmaceutical compounds may enter the environment by different routes such as discharge of treated wastewater, waste materials from landfill sites, and runoff from animal's waste[3]. Although pharmaceuticals are subjected to thorough testing before they are approved for human use, little research is available on the fate of pharmaceuticals once they have served their desired medicinal purpose[4]. Various physical and biological processes occurring in aquatic ecosystems may cause reduction of many pharmaceutical compounds, yet, trace concentration of human and veterinary pharmaceutical compounds as well as their metabolites have been detected in different water bodies like surface water, ground water and drinking water sources[3].

Some of these pharmaceuticals contain antibiotics which are taken by aquatic animals and absorbed into the plants through this water bodies, these plants are in turn harvested and consumed by both human and animals which possesses a great threat to the health. Resistance occurs when an antibiotic is no longer effective in killing or limiting bacteria growth. It can occur naturally or be acquired through previous exposure to antibiotics or through contact with another organism that is resistant. Antibiotics are effective in fighting against infectious diseases caused by bacteria and other microbes, almost all bacteria have become stronger and less responsive to antibiotic treatment. However, bacteria may become resistant by genetic mutation which is as a result of changes that occurs in the bacteria genetic material. Any bacteria that acquire resistant genes whether by spontaneous mutation or previous exposure to antibiotic have the ability to resist one or more antibiotic[5,6].

Current thinking promotes the idea that wastewater containing pharmaceuticals be treated before discharging into water bodies. Available chemical processes such as advanced oxidation processes can often degrade and decompose antibiotic molecules into simple compounds. These technologies and processes are however, very expensive and difficult to operate for complete elimination of these antibiotics, thus limited in applicability on an industrial scale[7,8,9], therefore there is urgent need for improving on the existing techniques. Physical techniques remain the most appropriate treatment option and adsorption is among the most efficient of these techniques for removing organic compounds from industrial effluents[10,11].

Adsorption is the accumulation of matter from a gas or liquid phase to the surface of an adsorbent, which could involve physical, chemical adsorption or mixed[12]. Adsorption process is very efficient, simple to design and operate and is relatively inexpensive and unaffected by the potential toxicity[12]. Silica gel is one among the most commonly used adsorbent in the adsorption process due to its high degree of micro porosity and enhanced adsorption properties. Although silica gel is an effective adsorbent, its application is limited due to its high cost and minimal decomposition which may cause more environmental problems. Also, most of these adsorption media are very costly, thus the use of low-cost adsorbents derived from agricultural and industrial solid waste for wastewater treatment has attracted much attention in recent years [13]. This waste material such as corn cobs, groundnut husks and rice husks are under-utilized and hence, they are readily available, in addition, the choice of a cheap precursor for the production of adsorbent means both considerable savings in the production cost and a way of making use of a waste material, thus reducing its disposal problem [13].

2. Materials and Methods

2.1. Preparation of Rice Husk Adsorbent

Rice husk was obtained from rice mill in Wurukum, New Bridge Road, Makurdi, Benue State, it was washed with distilled water to remove dust and dried at room temperature for 72 hours[14]. The dried husks were ground into powder, using a mortar and pestle and sieved through 20 um mesh size. The powdered husks were then ashed using a Ney M-252 Model muffle furnace at 600 ºC for 4 hours and cooled to room temperature. It was then treated with 200 mL portions of 1 M NaOH and heated at 80 ºC in 250 mL Erlenmeyer flasks for 1 hour with constant stirring. The solution was allowed to cool to room temperature and filtered through Whatmann filter paper (110 mm), the filtrate was treated with 1 M HCl with constant stirring, using a KJ 78 – 1 hot plate magnetic stirrer and measurement of pH using a HI 9024 Model pH meter to ensure that the pH was less than 10. The gel precipitated when the pH was less than 10. The gel obtained was aged for 24 hours. The gel was transferred into a beaker and dried using a Ney M-252 Model muffle furnace at 80 ºC for 12 hours to produce xerogels. Xerogel sample was ground and washed with distilled water. The sample was stored in airtight plastic bottles for further analysis[15].

2.2. Aqueous Solution of Ampicillin

1000 mg/ L stock solution of Ampicillin was prepared by dissolving 500 mg of ampicillin capsule in volume of distilled water distilled water and made up to mark in a 500 mL volumetric flask and was shaken and kept for serial dilution[16]. From the stock, working solutions of 80, 100, 120, 140 and 160 mg/L were prepared from appropriate aliquots diluted to the appropriate concentration.

2.3. Experimental Procedure

The rate of adsorption and equilibrium data was obtained from batch adsorption studies. This was done by varying contact time, adsorbent dosage, temperature, pH and concentration, so as to study the effect of the aforementioned on the adsorption of ampicillin on Rice Husk adsorbent.

2.4. Variation of Adsorbate Concentration

Several standard solutions with concentration of 80, 100, 120, 140 and 160 mg/L were prepared. 50 mL of each solution was added to 1.0 g of the adsorbent in different 100 mL flasks and agitated using a mechanical agitator at 25 ºC for 1 hour each. At the end of the time, the content of the flasks was filtered and contacted with sodium hydroxide and potassium permanganate and the absorbance of ampicillin were determined using the 7305 JENWAY UV-visible spectrometer [17,18].

2.5. Variation of Adsorbent Dosage

Ampicillin solutions of 50 mL each were added to 0.2, 0.4, 0.6, 0.8 and 1.0 g of the adsorbent in different 100 mL flasks, the flasks were agitated for 1 hour at 25 ºC on a Hy-2 Model mechanical shaker. The content of the flask was filtered and further contacted with sodium hydroxide and potassium permanganate and the absorbance of ampicillin were determined using the 7305 JENWAY UV-visible spectrometer[17].

2.6. Variation of pH Value

Absorbents of 1 g were weighed and poured into five separate conical flasks. Then 50 mL of 50 mg/L of the standard solution of ampicillin was added to each conical flask and their pH was adjusted to 3.0, 5.0, 7.0, 9.0 and 11.0 respectively. They were all placed on a mechanical shaker at 25 ºC for 1 hour. The filtrates were obtained and further contacted with NaOH and $KMnO_4$ and their ampicillin concentrations were determined using the 7305 JENWAY UV-visible spectrometer[18]. The results obtained are shown in figure 3.

2.7. Variation of Contact Time

Ampicillin solution of 50 mL each were transferred into different 100 mL flasks. 1 g each of the absorbent was weighed into the different flasks and agitated in a shaker at 25 ºC for 10, 20, 30, 40 and 50 mins respectively. After the mentioned time, the content of each flask was filtered and contacted with potassium permanganate and sodium hydroxide. The equilibrium concentration of the ampicillin in each of the filtrate was determined using the 7305 JENWAY UV-visible spectrometer[17]. The results obtained are presented in figure 4.

2.8. Variation of Temperature

Ampicillin solutions of 50 mL each were transferred into various 100 mL flask containing 1 g each of the adsorbent, corked and labeled for different temperatures 30, 35, 40, 45 and 50 ºC respectively. The mixture was heated and shaken to the appropriate temperature for 1 hour, the content of each of the flask was removed, filtered and contacted with potassium permanganate and sodium hydroxide and analyzed using the 7305 JENWAY UV-visible spectrometer[17]. The results obtained are shown in figure 5.

3. Results and Discussion

3.1. The Effect of Concentration

The concentration-dependent data for the adsorption of ampicillin is presented in figure 1. There is an increase in the adsorption of adsorbate from 80 mg/L to 100 mg/L and 120 mg/L to 160 mg/L due to active forces of attraction between the adsorbent and the adsorbate ion in solution which may have been active making the adsorption to increase[19]. This is also due to the fact that as the concentration is increased, more ions are available in the solution for the adsorption process[20]. The decrease in adsorption from 100 mg/L – 120 mg/L might be due to the fact that adsorption site was covered resulting to lesser availability of adsorption sites[21].

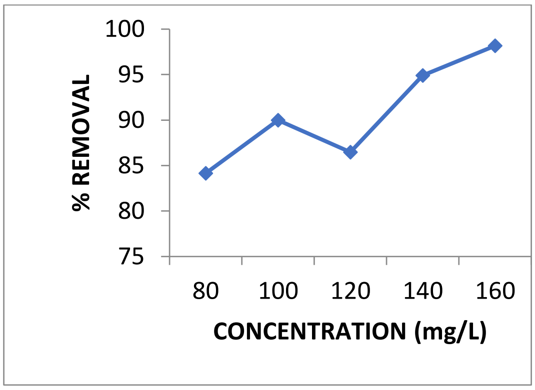


Figure 1: Effect of Concentration

3.2. Effect of Adsorbent Dosage

The effect of the adsorbent on the removal of ampicillin from aqueous solution was investigated by varying the dose of adsorbent from 0.2–1.0 g. it is expected that an increase in the dosage of adsorbent should yield a corresponding increase in the amount of the absorbate absorbed on the source of the absorbent since there will be more site for the adsorbate to be adsorbed. Therefore, competition for bonding sites between molecules of the adsorbate should decrease with increase in dose of adsorbent[17,22,23]. Nevertheless, from figure 2 this trend was inconsistent and therefore suggests that the use of rice husk adsorbent depends partially on its dosage in aqueous solution. Further increase of adsorbent dosage does not cause any significant change rather decreases the adsorption of the adsorbate. This may be due to unavailability of the exchangeable sites or surface area at the higher dosage of the adsorbent[21].

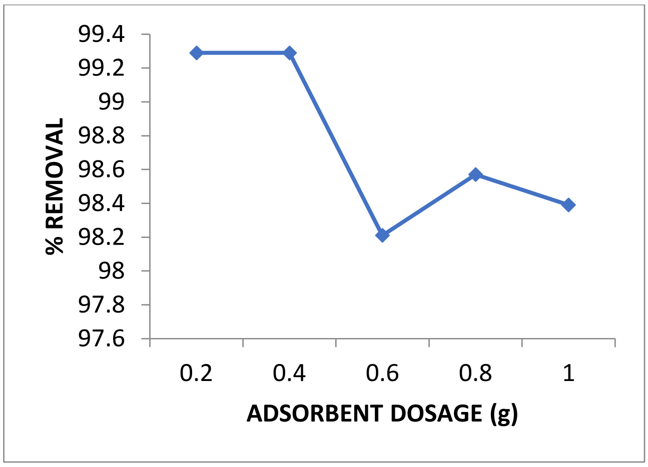


Figure 2: Effect of Adsorbent Dosage

3.3. Effect of pH Value

The effect of pH on the adsorption of ampicillin on adsorbent was studied as shown in figure 3. A decrease in the adsorption from pH of 3-5 and 9-11 was observed. This might be due to the fact that the surface of the adsorbent might have associated with hydronium ions (H_3O^-), by repulsive forces, to the surface functional groups, consequently decreasing the adsorption percentage of ampicillin. At pH 5-9 there was a corresponding increase in the deprotonation of the adsorbent surface, leading to a decrease in H^+ ion on the adsorbent surface. This creates more negative charges on the adsorbent surface, which favours adsorption of positively charge species and the positive sites on the adsorbent surface[19,21].

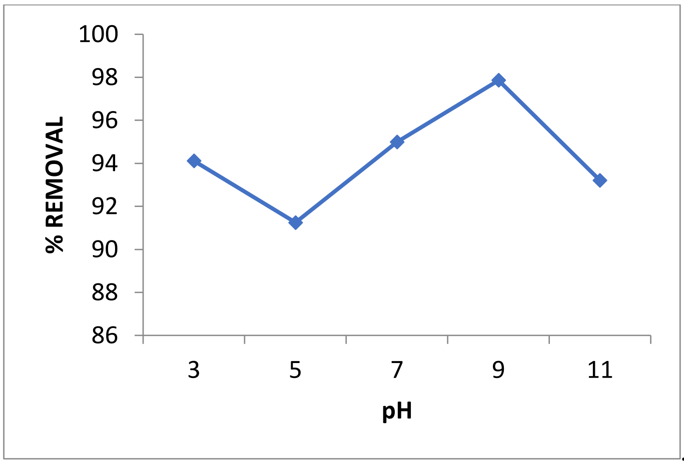


Figure 3: Effect of pH

3.4. The Effect of Contact Time

The experimental result on the effect of contact time in figure 4 shows a decrease in adsorption from 10 to 30 mins which implies that many adsorption sites were covered as the concentration increase from 10 to 30 mins, as opposed to the works of others researchers who had Rapid adsorption in the initial stages of the process, probably due to the increase in the concentration gradient between the adsorbed material in the solution and adsorbent[24,25,26]. There was an increase in adsorption from 40 - 50 minutes, which may be due to uncovered surface area of the adsorbents, since the adsorption kinetics depends on surface area of the adsorbents which is in accordance with Ligate etc. [21].

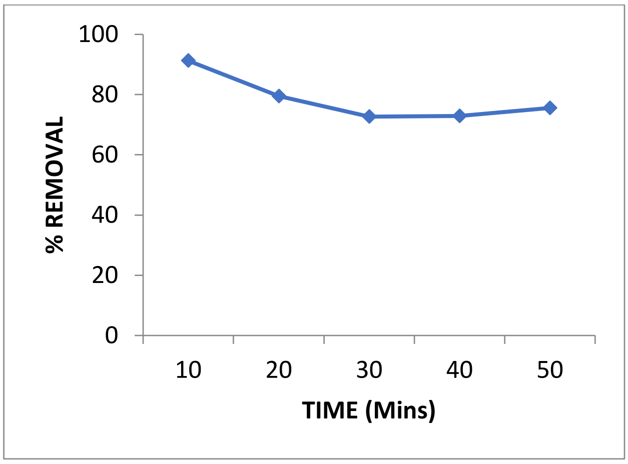


Figure 4: Effect of Contact Time

3.5. Effect of Temperature

The effect of temperature on the adsorption of ampicillin from aqueous solution was investigated by varying the temperature of adsorption between 30 ºC and 50 ºC as shown on figure 5. The data showed that with increasing temperature the amount of ampicillin absorbed on the surface of the adsorbent increases from 30-45 ºC. This can be attributed to active forces of attraction between the adsorbent and the adsorbate ion in solution which may have been active making the adsorption to increase[19]. At 50ºC the thickness of the boundary layer is expected to decrease due to the increased tendency of the ions to escape from the surface of the adsorbent to the solution phase hence there is bound to be weak adsorption interactions between the adsorbent and the adsorbate[17.] An increase in the temperature between 45 ºC and 50 ºC caused a proportional decrease in the amount of ampicillin adsorbed on the surface of the adsorbent. This decrease in adsorption capacity with increase in temperature indicates that the adsorption processes were exothermic in nature[21].

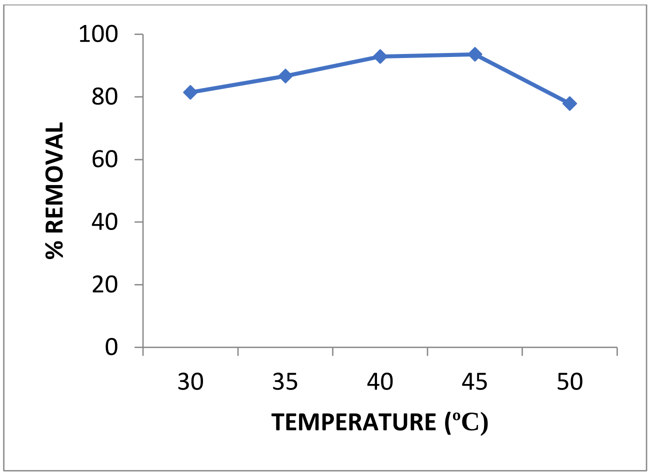


Figure 5: Effect of Temperature

3.6. Characterization

The Fourier Transform Infra-Red (FTIR) spectra are listed in figure 6.

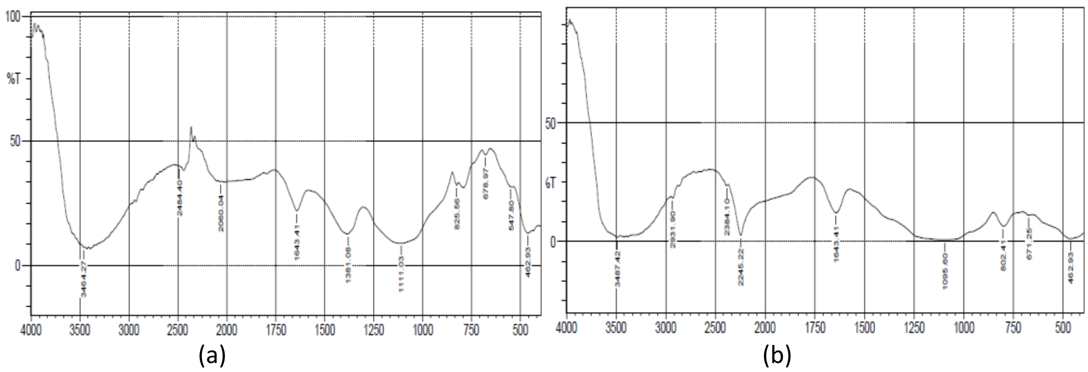
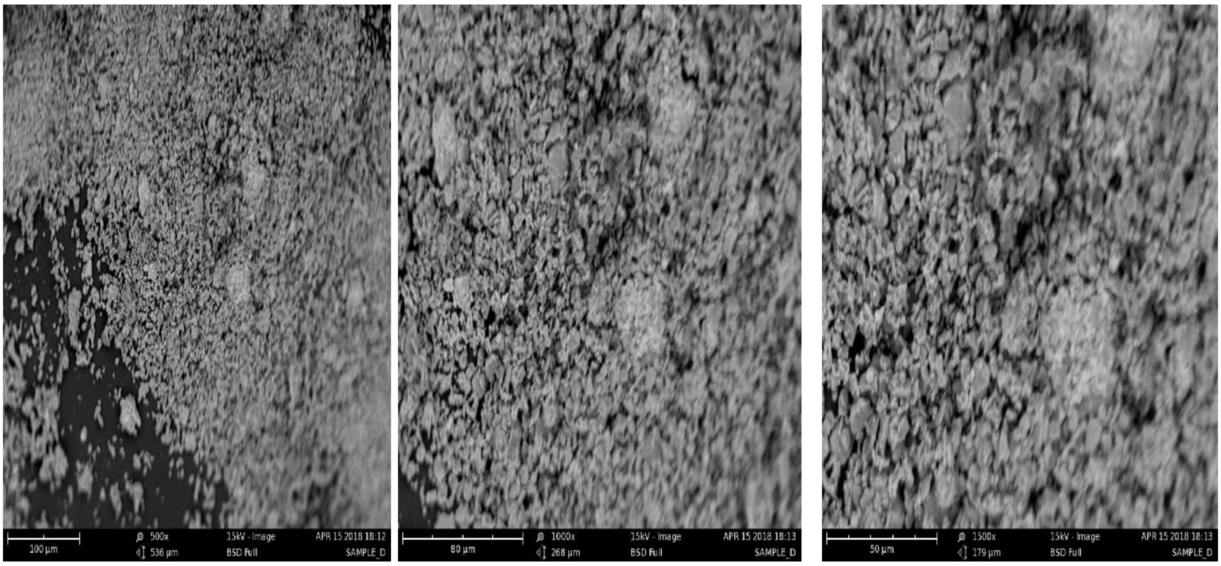


Figure 6: FTIR spectra. (a) uncontacted (b) contacted rice hush adsorbent

From the FTIR results, it was observed that peak at 648.97 cm^{-1} corresponding to stretching vibration of =C-H, 1111.03 cm^{-1} of C-H, 2060.04 assigned to CN and 3464.27 of O-H were shifted to 802.41 of =C-H, 2931.90 of C-H, 2384.10 of CN and 3487.42 of O-H. The FTIR spectra of the uncontacted and contacted rice husk adsorbent were recorded in the range of 450 cm^{-1} – 4000 cm^{-1}. The uncontacted rice husk adsorbent consists of peaks at 648.97 cm^{-1}, 1111.03 cm^{-1}, 2060.04 cm^{-1} and 3464.27 cm^{-1}. These peaks confirmed the presence of =CH, -CH, CN and OH in the uncontacted rice husk, which were shifted to higher peaks of 802.41 cm^{-1}, 2931.90 cm^{-1}, 2384.10 cm^{-1} and 3487.42 cm^{-1} corresponding to =CH, -C-H, CN and O-H. This change observed indicate the involvement of these functional groups in the adsorption process, suggestive of chemical adsorption. From the result above it was also observed that there is no complete shift in adsorption and also that the increase in the intensity of the peak suggest that there is an addition of antibiotics which is an indication of physical adsorption. This is in accordance with researcher[27].

3.7. Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) microstructure revealed the surface morphology of the adsorbent derived from rice husk. Images were obtained at 500x, 1000x and 1500x magnification as shown in image (a), (b) and (c). The SEM micrograph of adsorbent shows the existence of small black spots corresponding to the pore spaces like cylindrical holes. The very fine gel compound aggregate is surrounded by a great number of pores giving the impression of a sponge. This porous texture indicates a good adsorption capacity of the synthesized adsorbent. Although the different pretreatments used affected the chemical composition of the silica gel obtained, it seems that the structure and the morphology of these particles were not altered.



(a) (b) (c)

Figure 7: SEM images of rice hush adsorbent at (a) 500x magnification (b) 1000x magnification (c) 1500x magnification

3.8. Adsorption Isotherm

The equilibrium adsorption isotherm is one of the most important data to understand the mechanism for the adsorption of ampicillin. In this manner, the Langmuir, Freunlich and Temkin isotherm equations were used to interpret the experimental data. Langmuir Adsorption Isotherm explains quantitatively the formation of a monolayer adsorbent on the outer surface of the adsorbent in which no adsorption takes place after that. This isotherm is considered useful for monolayer adsorption onto a surface containing a finite number of identical sites[28]. The linear equation is given below:

$$\frac{1}{q_e} = \frac{1}{\beta q_m C_{eq}} + \frac{1}{q_m} \quad (1)$$

The linearized freundlich isotherm equation that corresponds to the adsorption heterogeneous surface is given as:

$$lnq_{eq} = lnk_f + \frac{1}{n}\ln C_{eq} \qquad (2)$$

where Ce is the equilibrium concentration of the solute (mg/L) and qe is the equilibrium adsorption capacity

The Tempkin Isotherm model has a factor that explicitly account for adsorbent adsorbate interactions by ignoring the extremely low and large value of concentration.

$$q_e = \frac{RTlnat}{bt} + \frac{RTlnC_e}{bt} \qquad (3)$$

The correlation coefficient of Langmuir, Freundlich and Tempkin for ampicillin adsorption on rice husk adsorbent is listed in table 1. This equilibrium data agrees with the Langmuir model which assumes that the adsorption on a homogeneous surface, i.e, the surface consist of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface[17].

Table 1: Correlation coefficient for Ampicillin on rice husk adsorbent

Adsorption Isotherm	R^2
Langmuir	0.811
Freundlich	0.705
Tempkin	0.639

4. Conclusions

The adsorption of ampicillin was carried out using batch adsorption studies which were conducted at various conditions such as temperature, pH, adsorbent dosage, concentration of the adsorbate and contact time. It was found that, the adsorption of ampicillin from aqueous solution depend on the solution adsorbent dose, contact time, concentration, pH and temperature. The adsorption obeys Langmuir adsorption isotherm because the R^2 value is close to the degree of unity.

Acknowledgments

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