Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

Treatment of Effluent Wastewater From Petrochemical Using Adsorbent from Waste Sugarcane Bagasse.

Uloko, N. M., Goodhead, T. O. and Ukpaka, C. P.
Department of Chemical /Petrochemical Engineering, Rivers State University of Science and Technology Port Harcourt, Nigeria. Email: maxwelluloko@yahoo.com

ABSTRACT
Wastewater is an environmental problem. The cost of treating wastewater is expensive. Identification of cheap and locally available materials will reduce the burden of wastewater treatment. Sugarcane bagasse is an agricultural wastes and adsorbent from it has been used in this research project. The adsorbent produced and the petrochemical wastewater samples were first characterized. The petrochemical effluent wastewater contains Fe, Cd, Cu, Pb, Ni, and Zn. The adsorption study was done by batch experiments. The rate of adsorptions of the metal increased with increasing contact time and adsorbent dosage. The percentage removal of the metal ions followed progressively in the order Fe > Ni> Cu> Pb> Zn> Cd. The equilibrium data obtained from the effect of temperature at30^{0}C, 60^{0}C, and 90^{0}C respectively were used to plot Langmuir and Freundlich isotherms. The separation factors, R_l calculated through Langmuir isotherm model confirmed favourable adsorption corresponds to fast kinetics obeying pseudo-second order type. The adsorption process fitted well for Langmuir adsorption isotherm model. The adsorbent was characterized using Scanning Electron Microscope (SEM) to obtain the pore and fibre Histogram. The Fourier – Transform infrared spectroscopy (FTIR) spectra provided insight on the functional groups present on the surface of the sugarcane bagasse adsorbent as OH (alcohols), OH (acids) and C=O (carbonyl). The adsorbent proved effective in removing heavy metal ions from the wastewater through adsorption .The values of separation factor R_l are similar to those typical of adsorbents from literature.

KEYWORDS: Treatment, Wastewater, Sugarcane Bagasse, Adsorbent, Adsorption, Isotherm

Cite This Paper: Uloko, N. M., Goodhead, T. O. & Ukpaka, C. P. (2022). Treatment of Effluent Wastewater from Petrochemical UsingAdsorbent from Waste Sugarcane Bagasse. *Journal of Newviews in Engineering and Technology*. 4(3), 104 – 118.

1.0 INTRODUCTION

The pollution of water by poisonous heavy metals is a serious environmental challenge, hence there is need to minimize the indiscriminate disposal of heavy metals and discover cheaper means of its removal from wastewater. One very promising and cheaper alternatives for eliminating heavy metals from wastewater is the use of nonconventional methods such as agricultural wastes, hence the need to carry out research on the possibility of applying agricultural wastes in curbing the potential dangers heavy metals pose to the public health if not properly handled. One of the past events of poisoning by heavy metal in the aquatic habitat occurred in Japan. This is one of the most severe kinds of chronic Cadmium poisoning caused by prolong exposure to Cadmium through ingestion. This incidence took place in Jinzu River basin in Toyama Japan due to pollution caused by a Zinc Mine situated nearby (Baba *et al.*, 2013). Heavy metals contamination and consequently poisoning also can be through food chain where an inorganic form of metal like Mercury get changed to methyl mercury and build up in the body of animals through food chain, particularly in fish. The fact that heavy metals have shown carcinogenic tendencies calls for research into possible preventions and management of pollutions caused by heavy metals (Moonis, 2007).

Heavy metals release into the environment has increased due to rise in industrialization and urbanization which poses serious pollution

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

problem to man and the ecological environment. An established fact is that many heavy metals constitute toxicity to human beings and other biotic factors of the ecosystem. Such metals include: cadmium, mercury, lead, copper, antimony, chromium, manganese (Ahsan, 2007). Heavy metal can be defined as any metallic chemical element with relatively high density (usually 5.0 or higher that of water) and is capable of causing poisonous effect even when the concentration is low. Mercury, lead and Arsenic are some of the heavy metals that are harmful to man. The main heavy metals covered by legislations are cadmium, lead and mercury (Paul *et al*, 2014).

Main sources of heavy metals include::Rubbish burning/incineration, for instance of medical wastes that contain toxic heavy metals, Waste disposal, Addition of lead to petrol, Burning of old painted surfaces, Mining activities, manufacturing of Radiator, Tanneries, Alloy industries, Batteries factories, Coal combustion, Phosphatic fertilizers, Water pipes, Dye, Textiles etc. (Vaibhav *et al*, 2017). Prolong exposure to heavy metals have adverse health effects. Humans can get exposed to heavy metals either through inhalation of air pollutants, consumption of contaminated drinking water, interactions with contaminated soils or waste from industries, or consumption of contaminated food, vegetables, grains, fruits, fish and shell fish can become contaminated by Storing metals from surrounding soil or water (Moonisha *et al*, 2014).

Some health challenges caused by exposure to heavy metals are cancer, organ damage, nervous system damage, and in severe cases can lead to death. These metals are particularly poisonous developing system of fetuses, infants and tender children. Lead and mercury easily permeate the placenta causing destruction to the fetal brain.

ATSDR which stands for Agency for Toxic Substances and Disease Registry in collaboration with the U.S environmental protection Agency has produced a priority list for 2001 called the "TOP 20 hazardous substance". The heavy metals in the lists are; Arsenic (1), Lead (2), Mercury (3) and Cadmium (7). There are 35 metals of interest, with 23 of them are heavy metals. Some of the commonly encountered toxic heavy metals include: Arsenic, lead, mercury, cadmium, iron. Toxicity can come from any of the metals (ATSDR, 2006). The need for safe and economical techniques for the elimination of heavy metals from contaminated water has called for this research work (Gunatilake, 2015). The work is to contribute in the search for readily available and less expensive adsorbents and their utilization possibilities, especially in the elimination of heavy metals from wastewaters. Sugarcane bagasse requires little processing, it is readily available and is a by-product or waste material from the sugar industry (Ezzat *et al*., 210). Therefore, it is of urgent importance to explore the possibilities of using agro-based inexpensive adsorbents in the removal of heavy metals. The following general methods may be employed to remove heavy metals, namely: chemical precipitation, ion exchange electro dialysis, membrane filtration, adsorption and co-precipitation/ adsorption methods (Ahsan, 2007).

The use of adsorbent to remove heavy metals is by adsorption which can be physio-sorption or chemisorption. Adsorption refers to a surface phenomenon that leads to mass transfer of a molecule from a fluid bulk to the solid surface. This process is governed by physical forces or by chemical bonds. Usually it is reversible, the reverse process is called desorption. In several cases, this process is described at the equilibrium by means of some equations that determine the amount of substance attached on the surface of the adsorbent given the concentration in the fluid. These equations are called isotherms, the most famous are the Langmuir and the Freundlich equations due to the dependence of their parameters on the temperature, which is one of the most important physical factors affecting adsorption process (Sparks, 2001.

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

This project work is concerned with the treatment of effluent wastewater to remove heavy metal using adsorbent from sugarcane bagasse. The need for safe and economical techniques for the elimination of heavy metals from contaminated water has called for this research work (Gunatilake, 2015). The work is to contribute in the search for readily available and less expensive adsorbents and their utilization possibilities, especially in the elimination of heavy metals from wastewaters. Sugarcane bagasse requires little processing, it is readily available and is a by-product or waste material from the sugar industry (Ezzat *et al*., 210). Therefore, it is of urgent importance to explore the possibilities of using agro-based inexpensive adsorbents in the removal of heavy metals.

The need for cheaper and readily available alternative methods besides the conventional ones, for the elimination of heavy metals from contaminated water necessitated this research work. The work is to contribute in the search for readily available and less expensive adsorbents and their utilization possibilities, especially in the elimination of heavy metals from waste waters. Sugarcane bagasse requires little processing, it is readily available and is a by-product or waste material from the sugar industry. Therefore, it is of urgent importance to explore the possibilities of using agro-based inexpensive adsorbents in the removal of heavy metal. This project is particularly important because of the poisonous nature of heavy metals such as Lead and which Nigeria is also prone to its danger effects. Leaded fuel has been banned, but the work of unscrupulous Nigerians do not make this legislation effective. Lead poisoning was reported in Zamfara, Northern Nigeria in the year 2010 in which many Nigerians died. Nigeria has high deposits of lead. Battery industries are also in Nigeria. The unhealthy disposal of medical waste materials has worsened the situation also

Gunatilake (2015) worked on the Methods of Removing Heavy Metals from Industrial Waste water. Some physico-chemical extraction processes such as; adsorption on new adsorbents, ion exchange, membrane filtration, electrodialysis, reverse osmosis, ultrafiltration and photo catalysis were discussed. Their usefulness and limitations in application were evaluated. According to Gunatilake, in the processes of biological treatments microorganisms play important role of settling solids in the solution. He explained that activated sludge, trickling filters, stabilization ponds have wide applications in treating industrial wastewater. He stated bio adsorption as a new biological method and various low-cost bio adsorbents are now used for maximum removal of heavy metals from wastewater. Even with high cost of chemical method, the chemical treatments is one of the most efficient treatments for toxic inorganic compounds released from various industries which cannot be removed by biological and physical methods.

Ezzat *et al.* (2010) also researched on the "reactivity of sugar cane bagasse as a natural solid phase extractor" for preferential removal of Fe^{3+} and heavy metals from natural water samples". His work introduced the feasibility of using sugarcane bagasse (SCB) which is a sugarcane industry waste as a selective natural solid extractor for Fe^{3+}. The order of metal uptake abilities in lmol g^1 for the extraction of six metal ions which he tested from aqueous solution using static technique is $Fe^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Cd^{2+} > Co^{2+}$. Since sugarcane bagasse shows remarkable binding characteristics for Fe^{3+}, special attention was given to optimizing its uptake and studying its selectivity behaviours under both static and dynamic conditions. In this respect, batch experiments were carried out at the pH range 1.0–4.0, initial concentration of metal ion (10–100 mol/volume), weight of phase (25, 50, 75, 100, 125 and 150 mg) and contacting time (10, 30, 45, 60, 90, 120 and 150 min). FTIR spectra of Sugarcane bagasse before and after uptake of Fe^{3+} were recorded to probe into the nature of the functional groups present and responsible for binding of Fe^{3+} onto the natural biosorbent. The

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

equilibrium data were better fitted with Langmuir model ($r^2 = 0.985$) than for Freundlich model in which ($r^2 = 0.934$). Moreover, Fe^{3+} sorption was rapid and completed within 60 min. The adsorption kinetics data were best fitted with the pseudo-second-order type.

Mohammed (2017) carried out research on the possibility to remove heavy metals from aqueous solutions by the use of natural agricultural wastes called orange peels activated carbon. In the study his aim was to determine the applications of adsorption isotherms models during the adsorbent behaviour of orange peel activated carbon to remove $Pb^{+2,}$ Ni^{+2}, Cr^{+3} and Cd^{+2} ions. The micropore area, specific surface area, and the dependence of the adsorption on pH value, contact time and dosage of orange peel activated carbon were investigated. From isotherm studies both Langmuir and Freundlich adsorption isotherms well fitted models and confirms that adsorption of metals ions is one layer adsorption and revealed highly efficient orange peel activated carbon in the removal process for the metal.

Moonis (2008) also worked on "heavy metal pollution and its control through nonconventional adsorbents". According Moonis several low-cost adsorbents have been studied to remove and recover toxic metals like Ni, Cr, Zn, Cu, Pb, Cd etc. Atomic. Adsorption of metal ions occurred in the order Pb (II) > Zn (II) >Cd (II) the highest adsorption of Pb (II) was (100%) and occurred at pH 7. The adsorption at equilibrium followed the Freundlich adsorption isotherm. The adsorptive capacity of pyrolusite has been performed by removing lead from synthetic wastewater. 100% and 96% removal of Lead was achieved from synthetic wastewater containing 5 mg/l and 120 mg/l of Pb(II) respectively at pH 7. Phosphate enhanced saw dust proved remarkable increase in adsorptive capacity of Cr (VI) when compared to untreated sawdust. The adsorption process was pH dependent. 100% adsorption of Cr (VI) was occurred in the pH range < 2 for the initial Cr (VI) Concentration of 8-50 mg/l used. The results for the various adsorbent doses at pH 2 confirmed Langmuir adsorption isotherms model. The ability of fruit peels of orange to remove Zn (II), Ni (II), Cu (II), and Pb (II) were investigated and the adsorption was in the order Ni (II)>Cu (II)>Pb (II)>Zn (II).

The past works on the use of agricultural wastes (sugar cane bagasse) in the removal of heavy metal did not conduct experiment at various temperatures so as to identify the effect of temperature on the process. In particular reference to the use of sugarcane bagasse, no much work has been done on the effect of temperature on the adsorption process. No adsorption isotherm was made of the use of Sugarcane bagasse for the removal of heavy metal. Sugarcane bagasse was only tried on few selected heavy metals in prepared aqueous solution samples. The objectives of this research include: characterization of wastewater sample, preparation of adsorbent from sugarcane bagasse, experimentations on the factors affecting adsorption process, kinetic and isotherm studies of the adsorption process.

2 MATERIALS AND METHODS

2.1 Materials

The materials required in this research includes: Wastewater sample, Sugarcane Bagasse, Atomic Absorption Spectrophotometer, Methanol, Zinc chloride, Beaker, Measuring Cylinder, Distilled water, Grinder, Hot Plate, Pipette, COD Reagent, pH Meter Turbid meter, Colorimeter, Gas Chromatograph (GC), Fourier Transform Infrared Spectrometer (FTIR), Scanning Electron Microscope (SEM), Weighing Scale.

2.2 Methods

2.2.1 Collection and Analysis of Wastewater Sample

Industrial waste water sample was collected from the effluent of a petrochemical plant. The following analysis were conducted on the wastewater sample: AAS, GC, and pH, TSS, COD and Turbidity. The waste water sample

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

was characterized for the heavy metals present and their respective concentrations using 'An Analyst 200' model atomic adsorption spectrophotometer (AAS). Other properties of the waste water sample were also determined using various measuring equipment ranging from colorimeter (model: DR1890), turbid meter (model: 2100N), gas chromatography (GC, model: 7890A), COD digester (model: DB3A), pH *meter (model: 611)* etc.

2.2.2 Preparation of Adsorbent (Sugarcane Bagasse Activated Carbon)

The Sugarcane bagasse used was obtained from the remains of sugarcane after eating and was thoroughly washed with distilled water and soaked in methanol for 18 hours so as to free the sugarcane bagasse of impurities that may interfere with the adsorption results and to remove colour. Then the sugarcane bagasse was dried in the electric oven at 80°C (Mohamed *et al*, 2017). This drying by heating helps to remove the methanol from the carbon. After drying, it was crushed and carbonized at 400°C for 15 minutes and afterward activated using 1.0M $ZnCl_2$ at 500°C for 2 hours (Mohamed *et al*, 2017). It was cool at room temperature and sieved to a 1.0 mm mesh size. The adsorbent was characterized for functional group present using Fourier Transform infrared (FTIR, model: M530USA FTIR). The Adsorbent was characterized for surface properties using Scanning Electron Microscope (SEM, model: quanta FEG M450 with EDX analysis (Apollo X-EDAX)). UV-visible Spectrophotometer (Apel 3000UV) was used to conduct UV-visible Spectrophotometric analysis on the sample.

2.2.3 Effect of the Dosage of Adsorbent (Sugarcane Bagasse) on the Adsorption of Heavy Meta

In order to verify the effect of quantity of the sugarcane bagasse on the adsorption of the heavy metal, the following experimental steps were taken: 50mg, 100mg, 150mg and 200mg of sugarcane bagasse was placed in four (4) different beakers respectively. 75ml of the waste water sample was then added to the contents of each of the four beakers and allowed to stand for the period of 50 minutes with periodic stirring. The contents of the beakers was then filtered and the filtrates collected in different beakers after 50 minutes. The filtrates was then taken for analysis of the absorbance using AAS. The values of the absorbance was converted to concentrations and recorded in table.

$$\text{Concentration} = \frac{\text{sample absorbance}}{\text{standard absorbance}} \times \text{conc of standard} \times \text{dillution factor} \quad (1)$$

2.2.4 Effect of Contact Time on Adsorption of heavy metal onto Sugarcane Bagasse

2.5g of sugarcane bagasse was added each to five different beakers labeled 1 to 5, then 75ml of the waste water sample was added to each of the contents in the beakers and allowed contact times (minutes) of 10, 20, 30, 40 and 50 respectively with periodic stirring. After which they were filtered, and the filtrates collected for AAS analysis for concentration of the metal ions present. 0.5ml of conc. HCl was added to each filtrate to keep the ions in solution form, and the solutions were then warmed, cooled and analyzed using AAS Mohamed *et al.*, (2017).

2.2.5 The Effect of Temperature on Adsorption of the Metal Ions Using Sugarcane Bagasse

1.5g of sugarcane bagasse was placed in three (3) different beakers. 100ml of the waste water sample each was taken and poured into the three beakers each. One beaker was placed in the water bath at 30°C and heated for 20 minutes and the absorbance of the filtrates taken and recorded. The second beaker was placed in water bath at 60°C and heated for 20 minutes and the absorbance of the filtrates recorded. Then, the last beaker was placed on the water bath at 90°C and heated for 20 minutes and the absorbance of the filtrates recorded (Mohamed *et al.*, 2017).

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

2.2.6 The kinetics Studies of the Adsorption Process

Calculation of the equilibrium constant of adsorption k_o at equilibrium

$$Ko = \frac{\text{concentration of adsorbate in adsorbent}}{\text{concentration of adsorbate in aqueos solution}} \quad (2)$$

(Catena *et al.*, 1987).

Calculation of the Gibb's Free EnergyΔG^0, of the process

$$\Delta G^0 \text{ (KJ/mol)} = \Delta G^0 = -RTlnk_o \quad (3)$$

2.2.7 The Isotherm Studies of the Adsorption Process (Langmuir, Freundlich)

Langmuir: $$\frac{C_e}{Q_e} = \frac{1}{Q_m} b + \frac{C_e}{Q_m} \quad (4)$$

Freundlich: $$\log Q_e = \log K_f + \frac{1}{n} \log C_e \quad (5)$$

C_e = equilibrium concentration, mg/l

Q_m and b = Langmuir constants

K_f and n = Freundlich constants

Q_e = amount adsorbed at equilibrium, mg/g

2.2.8 Adsorption Capacity and Removal Efficiency of Heavy Metal ions

The adsorption capacity by activated carbons is given below (Horsfall *et al.*, 2006; Zulkali *et al.*, 2006):

$$q_e = \frac{(C_0 - C_e) \times V}{M} \quad (6)$$

$$R\% = \frac{(C_0 - C_e) \times 100}{C_0} \quad (7)$$

Where; C_0 is the initial metal ions concentration, Ce is the concentration of metal ions in solution (mg/L) at equilibrium, Ct is the concentration of metal ions in solution (mg/L) at time, t in solution, V is Volume of initial metal ions solution used (L) and M is mass of adsorbent used (g).

3.0 RESULTS AND DISCUSSION

3.1 Wastewater Characterization

The wastewater sample from the petrochemical effluent was analyzed for heavy metal ions using atomic absorption spectrophotometer (AAS) in which Fe, Cd, Cu, Pb, Ni and Zn were present in the concentrations (mg/l) 0.7821, 0.0295, 0.0227, 0.0355, 0.3706 and 0.9780 respectively. The petrochemical effluent wastewater has pH of 9.62 confirming that the wastewater sample is alkaline (Mohamed et al., 2017). The turbidity of the sample was obtained as 10. The wastewater sample has total suspended solid (TSS) of 30mg/l. the COD was measured as 90mg/l. The aromatics was nil and the phenolic composition was less than 1ppm. This is shown in Tables 1 and 2.

Table 1: Concentrations of the Various Metal ions in the Wastewater Sample as Analyzed Using AAS

Metals	Sample concentration, mg/l	WHO Effluent Standard (mg/l)
Cu	0.0227	1.000
Cd	0.0295	0.005
Zn	0.9780	5.000
Fe	0.7821	0.100
Ni	0.3706	1.000
Pb	0.0355	0.050

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

Table 2: Results from Characterization of the Wastewater Sample

S/N	Property	Value	WHO Effluent Standard (mg/)
1	pH	9.62	6.0-9.0
2	Total Suspended Solid TSS	30mg/l	30
3	Turbidity	10	550
4	Chemical Oxygen Demand	90mg/l	140
5	Phenols	<1ppm	1-5
6	Aromatics	Nil	

3.2 Adsorbent Characterization

The findings with regards to the characterization of the sugarcane bagasse adsorbent is presented in Tables 3, 4 and Figures 1, 2, 3 below. The moisture content was 9.74%, Lignin content was 10.30%, Hemicellulose was 4.99% and the Ash content was 8.17%. These compositions are similar to those stated in the literature by Ezzat Solimon and his colleagues (Ezzat *et al*, 2010). The following metals; Manganese, Sodium, Potassium, Aluminum, Molybdenum, Silver and Silicon were found in the concentrations of 0.154ppm,4.783ppm,4.984ppm,0.393ppm , 0.178ppm, 0.051ppm and 0.433ppm respectively. The Fourier-Transform Infrared Spectroscopy (FTIR) was also used to obtain the spectra as shown in figure 1. The FTIR spectra was obtained at frequency region of 4,000 – 600 cm^{-1} and co-added at 32 scans and at $4cm^{-1}$ resolution. FTIR were displayed as transmittance values. Functional groups give different peaks in different substances (Mohamed et al., 2017). It can be observed from the FTIR spectra displayed: the peak (3360, 56687) at wavelength between 300-3500 Cm^{-1} gives OH (alcohols), peak (1625, 46826) at wavelength 150-200cm^{-1} is C=O (carbonyl) group and peak (2879, 58635) at wavelength 2500-3000 cm^{-1} represents OH (acids) (broad peak). UV-visible spectrophotometric analysis was conducted on the sample using a UV-visible spectrophotometer (Apel 3000UV) with a slit width of 2mm, using a 10-mm cell at room temperature. The extract was examined under visible and UV light in the wavelength ranging from 200-1100nm. The scanning Electron Microscope (SEM) was used to measure the surface properties of the adsorbent as represented by pore Histogram and Fibre Histogram in Figures 3 and 2 respectively. The maximum pore Area was 448.13 μm^2. From the fibre histogram obtained, the fibre length were in the range 1.26µm, 4.21µm and 18.09µm.

Table 3: Results from Characterization of the Sugarcane Bagasse

S/N	Parameters	Value (%)
1	Cellulose	13.114
2	Lignin content	10.301
3	Moisture Content	9.740
4	Hemicellulose	4.987
5	Ash Content	8.170

Table 4: Results from Characterization of the Sugarcane Bagasse

S/N	Parameters	Value
1	Manganese	0.154ppm
2	Sodium	4.783ppm
3	Potassium	4.984ppm
4	Aluminium	0.393ppm
5	Molybdenum	0.178ppm
6	Silver	0.000
7	Silicon	0.433ppm

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

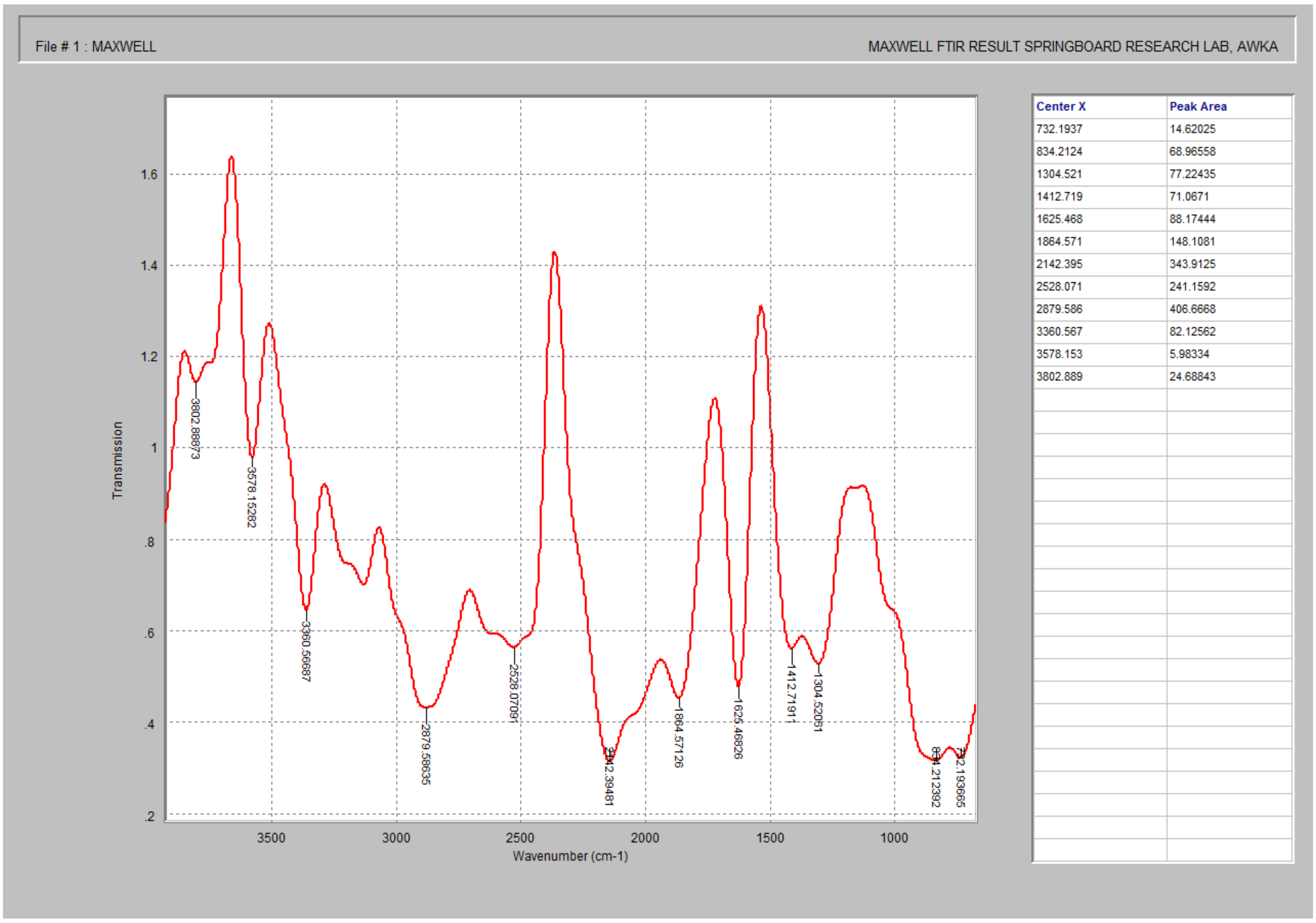

Figure 1: Results of FTIR Conducted on the Sugarcane Adsorbent

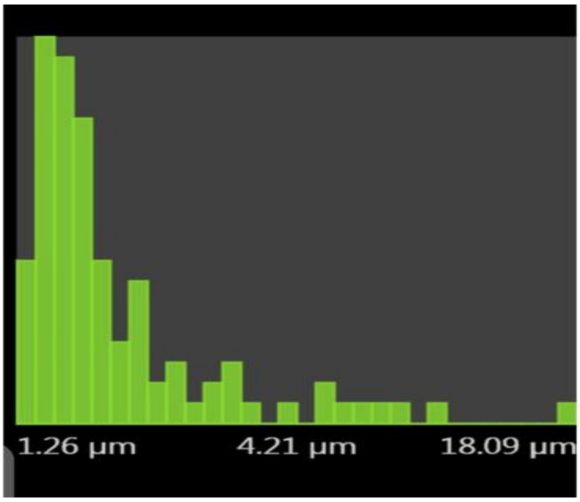

Figure 2: SEM Scan – Fibre –Histogram of the Sugarcane Bagasse

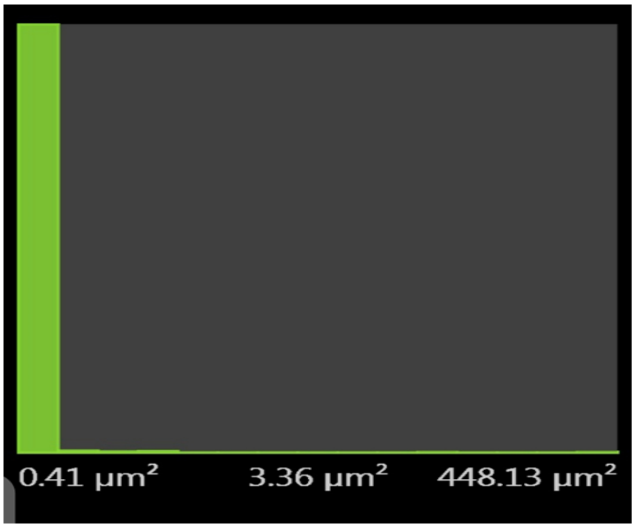

Figure 3: SEM Scanning Electron Microscope Pore- Histogram

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

3.3 Effect of Adsorbent Dosage on Adsorption of the Metals

This was achieved by varying sugarcane bagasse concentrations of (50mg, 100mg, 150mg and 200mg) for the metal ions initial concentrations (Mohamed, *et al.*, 2017). The percentage of adsorption increases with increasing sugarcane bagasse concentration as shown in Figure 4 below. It can be observed from Figure 4 that when sugarcane bagasse used was 50mg, the percentages (%) of the metal ions Fe, Cd, Cu, Pb, Ni and Zn removed were 3.92, 4.00, 13.13, 16.09, 4.02 and 26.15 respectively. As the concentration of the sugarcane bagasse was changed to 150mg, the removal (%) was 27.50, 23.34, 34.83, 50.05, 35.56 and 38.17 respectively. The Figure 4 reviewed that at the maximum concentration of adsorbent, 200mg, the respective percentage removal of the metal ions were 54.34, 30.55, 47.86, 50.05, 51.00 and 38.8. This observation can be attributed to increased sugarcane bagasse adsorbent surface area and availability of more adsorption sites.

It can be observed that the adsorption of Pb and Zn had become relatively constant suggesting that the ions were no longer been removed or were almost completely removed from the waste water onto the sugarcane bagasse. This suggests an equilibrium condition. At 150mg of the adsorbent the two metals ions concentration remain fairly constant. The other metals had not shown signs of reaching equilibrium

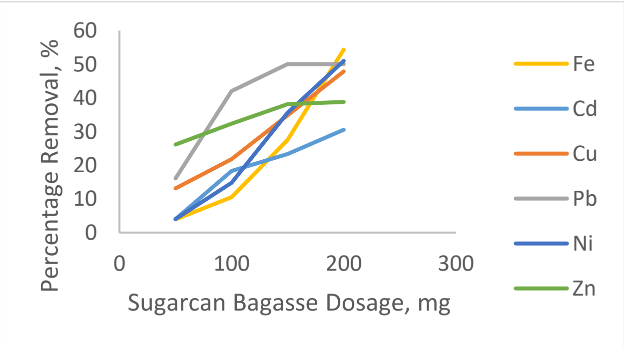

Figure 4: Effect of the Concentration of Sugarcane Bagasse on the Adsorption of Heavy Metals

3.4 Effect of Contact Time on Adsorption of the Metals

The experimental results of adsorption of the various heavy metal ions (Fe, Cd, Cu, Pb, Ni and Zn) from the wastewater sample on sugarcane bagasse adsorbent at initial concentrations (mg/l) of the metals 0.0560, 0.3319, 0.1014, 0.0141, 0.0402 and 0.3175 respectively at various contact times (minutes) are shown in Figure 5 below. The data collected and plotted in the graph shows that the percentage adsorption of the heavy metal ions increases progressively with increasing contact time while the concentrations of the ions in the wastewater filtrates decreases as the contact time increases, the factor responsible for this is the prolonged time of contact between the adsorbent surface and the metal ions (Mohamed., 2017) This is because, besides the dependence of adsorption on initial concentration of the adsorbent, the adsorption of the heavy metal ions onto the adsorbent depends also on the contact time, this is consistent with results obtained in literature by Mohammed and his colleagues on their work on bio sorption Mohamed *et al.*, (2017). It can be observed from Figure 5 that after 10 minutes contact time, the percentage removal of the various metal ions were respectively 32.87%, 2.98%, 17.44%, 24.08%, 9.92% and 30.47% for Fe, Cd, Cu, Pb, Ni and Zn . After 20 minutes it was 40.17%, 8.07%, 30.48%, 42.06%, 27.50% and 33.02% respectively for Fe, Cd, Cu, Pb, Ni and Zn ions. At the end of experimental time of 50 minutes the percentage removal of the heavy metal ions were 75.90%, 32.58%, 60.90%, 66.04%, 53.69% and 45.25%,

This observation confirms the fact that allowing more contact time is providing opportunity for longer contact time that favour more transfer of the heavy metal ions onto the adsorbent surface until equilibrium is achieved or the ions in the waste water is almost finished.

Adsorption of metal ions Zn, Cd and Ni had become constant, between the contact time of 40 to 50 minutes, indicating no further adsorption of these metals occur.

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

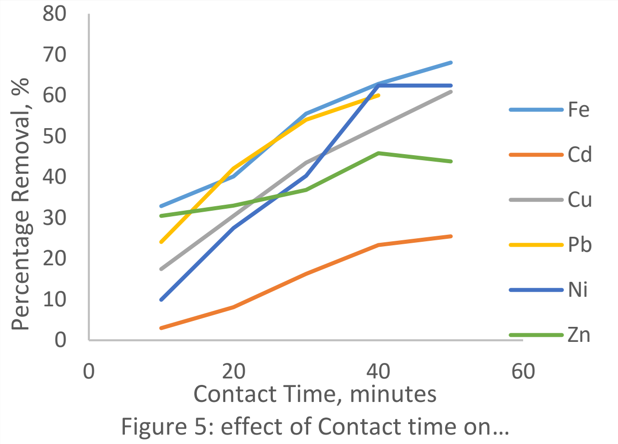

Fig. 5: Effect of Contact Time on the Adsorption of the Heavy Metals

3.5 Effect of Solution Temperature on Adsorption of the Metals

The Figure 6 below shows the effect of temperature on the adsorption of the metal ions by the adsorbent. It can be observed that the adsorption of heavy metal ions by sugarcane bagasse increases with increase in temperature of the wastewater solution from 30^0C to 90^0C. the Figure 6 shows that for the initial concentrations of the metal ions at 30^0C the removal of metals were 55.98%, 10.17%, 39.16%, 52.06%, 32.08% and 33.40% respectively for Fe, Cd, Cu, Pb, Ni and Zn. At 90^0C the removal were 75.90%, %, 32.58%, 60.90%, 66.04%, 53.69% and 45.25% respectively for the metals. It can be observed from Figure 6 of 2.5g adsorbent concentration that the adsorption of Cd and Pb reached Saturation whereby the percentage removal of the respective metals at 60^oc and 90^Oc shows no tangible difference. At this elevated temperature the adsorbate molecules get removed from the adsorbent by an opposite process called desorption. This confirms the fact that the adsorption of many metals are inversely proportional to the solution temperature at such elevated temperature.

The factor of temperature favours Ni, Zn and Cu more as there is more tendencies for their adsorptions at further temperature as depicted by Figure 6.

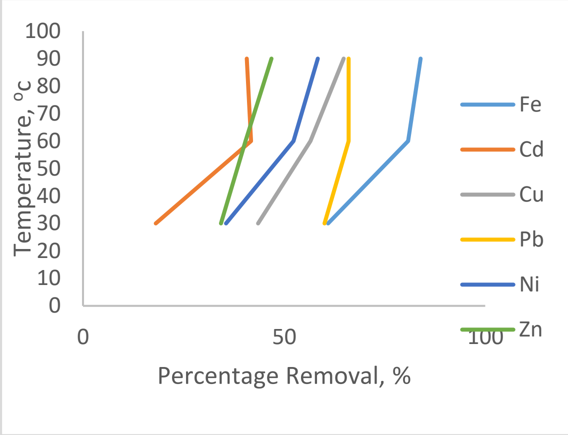

Figure 6: Effect of Temperature on the Adsorption of Heavy Metals by Sugarcane Bagasse

3.6 The Adsorption Isotherms of the Adsorption Process

The purpose of the adsorption isotherm is to relate the adsorbate concentrations in the bulk solution and the adsorbed amount at the interface (Demir *et al*, 2002). The experimental data were analyzed according to the linear form of the Langmuir and Freundlich isotherms. Here C_e is the equilibrium concentration (mg/L). Q_e is the amount adsorbed at equilibrium (mg/g) and Q_m and b are Langmuir constants related to the adsorption efficiency and energy of adsorption respectively. The linear plots of C_e/Q_e versus C_e suggests the applicability of the Langmuir isotherms (Figures 7, 8, 9, 10, 11 and 12). The values of "Q_m" and "b" were determined from the slope and intercept of the isotherm plot. From the results, it is clear that the values of adsorption efficiency Q_m and adsorption energy b of the sugarcane bagasse vary with increasing temperature.

To confirm the favorability of the adsorption process, the separation factor (R_L) was obtained and presented in Table 5. The values were found to be between 0 and 1 which confirm that the ongoing adsorption process is favorable (Treybal, 1985). The data fitted well for Langmuir model and better than the Freundlich model.

The Freundlich equation was also employed from the adsorption of the metals using sugarcane bagasse. K_f and n are constants incorporating all factors affecting the adsorption capacity and intensity of adsorption. The linear plot of log Q_e versus log C_e shows that the adsorption of the metals follows the Freundlich isotherm also. Observing freudlich isotherms from figures 13-15 it can be seen that for some metals the plots are straight line while for others they are not straight. For straight lines, the Freudlich isotherm is valid. Like for Cd, Cu and Pb. Freudlich isotherm is not valid at high pressure.

Table 5: Langmuir Isotherm Results

Metals	Statistical constants		parameters	
	R^2	R_l	Q_m	B
Fe	0.9947	0.762	0.4000 (2.5)	0.21
Cd	0.9929	1.000	0.0001(100)	
Cu	0.9740	1.000	0.0102(98)	0.1
Pb	0.9976	0.986	0.3960(2.5253)	0.4
Ni	0.9815	0.971	0.0800(12)	1.5
Zn	0.9927	0.855	0.1733(5.7692)	1.8

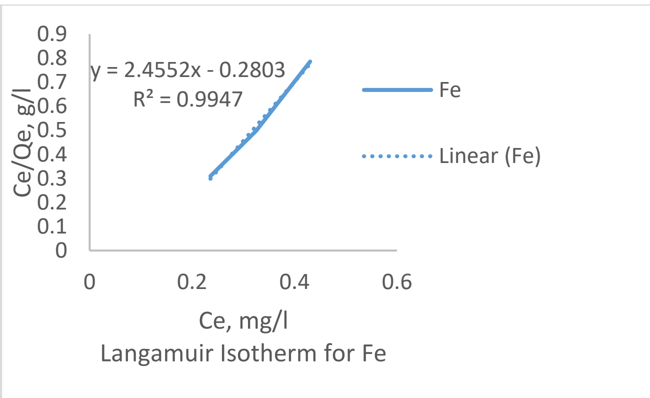

Figure 7: Langamuir Isotherm for Fe

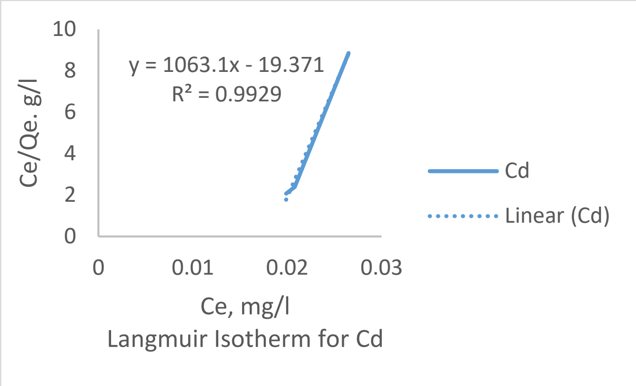

Figure 8: Langamuir Isotherm for Cd

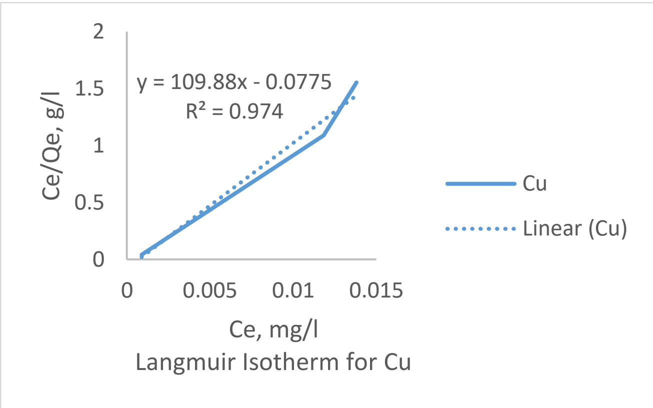

Figure 9: Langamuir Isotherm for Cu

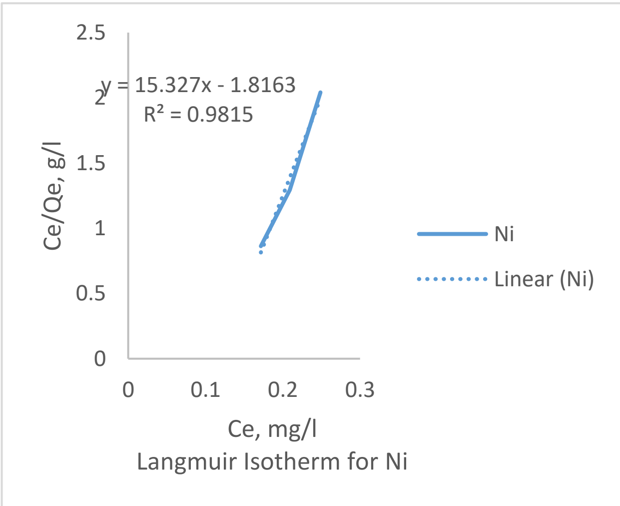

Figure 10: Langamuir Isotherm for Pb

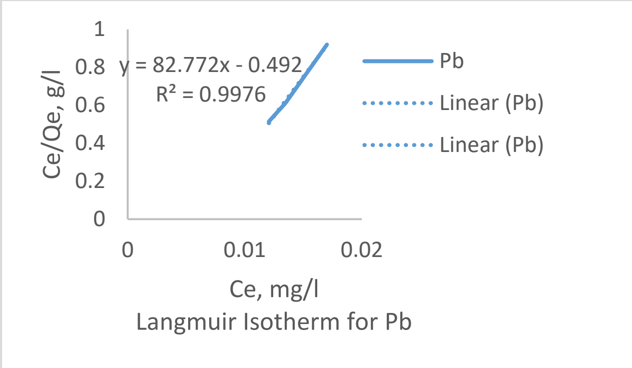

Figure 11: Langamuir Isotherm for Ni

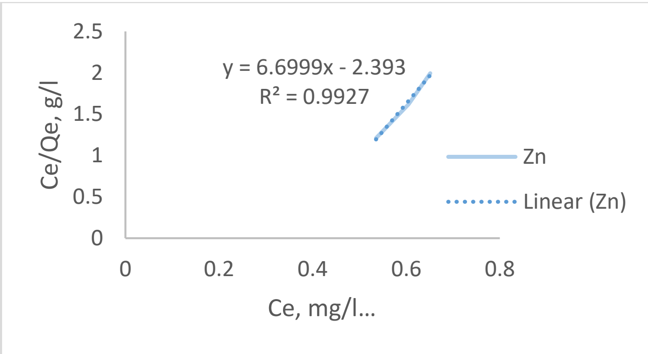

Figure 12: Langamuir Isotherm for Zn

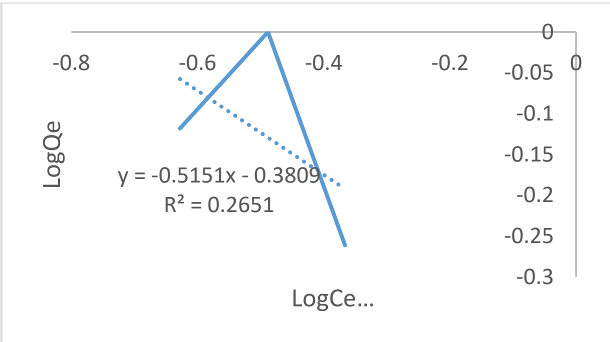

Figure 13: Freudlich Isotherm for Fe

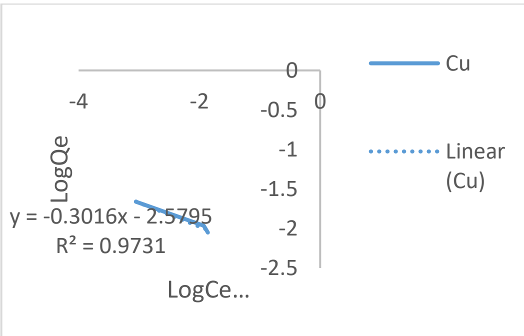

Figure 14: Freudlich Isotherm for Cu

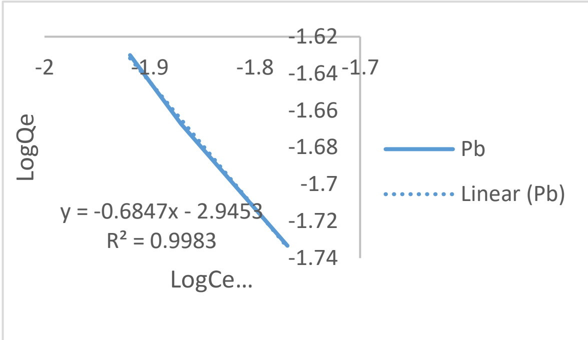

Figure 15: Freudlich Isotherm for Pb

3.7 Kinetics of the Adsorption Process

The kinetics of the process gives useful information about the rate of solute uptake in adsorption process, which in turn governs the residence time of sorption process (Ahsan, 2007). It is one of the important characteristics in defining the efficiency of sorption in this study; the kinetics of the heavy metals removal was carried out to understand the behaviour of this low-cost sugarcane bagasse adsorbent. The values of the kinetics of adsorption presented in Table 13 above Shows that the value of the equilibrium constant, K_0 increases progressively with rise in temperature. This further confirms that the efficiency of the removal of the heavy metals ions using sugarcane bagasse adsorbent is efficient and highly dependent on temperature. The value of K_0 is highest for Fe at 90^oc and lowest for Ni, suggesting that adsorption of Fe is most favoured and Ni is least.

The thermodynamic parameters such as change in Gibb's free energy (ΔG^0) KJ/mol was determined at 30^0C, 60^0C and 90^0C for all the metal ions present with the calculated values of $K_{0.}$ The positive values of ΔG^0 Table 13 for Cd and Zn ions shows that the lead ion adsorption is non-spontaneous Using sugarcane bagasse adsorbent. From the table it can be observed that the ΔG^0 for Fe and Pb are negative showing that the adsorption of the two metals are spontaneous in nature. The ΔG^0 values for Ni and Cu were positive at the lower temperature of 30^OC and changed to negative at 90^OC confirming that it started non-spontaneously but became

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

spontaneous at higher temperature. The values of ΔG^0 also shows the extent to which the adsorption process is favoured. The value of ΔG^0 decreases progressively with rise in temperature indicating that as the temperature is increasing the adsorption process becomes more favoured (Yu, 2009)

Table 6: The Values of Kinetics of Adsorption, k₀ and Change in Gibb's Free Energy, ΔG^0 for the Adsorption of Metal Ions by Sugarcane Bagasse

Iron (Fe)

T^{0}C	K_0 (m^{-2}s^{-1})	ΔG^0 (KJ/mol)
30	1.2712	-605.5210
60	2.0102	-1933.2121
90	3.1494	-3462.4574

Cadmium (Cd)

T^{0}C	K_0 (m^{-2}s^{-1})	ΔG^0 (KJ/mol)
30	0.1132	5488.5055
60	0.4100	2468.5818
90	0.4832	2195.1746

Cupper (Cu)

T ^{0}C (ms^1)	K_0	ΔG^0 (KJ/mol)
30	0.6434	1110.1918
60	0.9190	233.8712
90	1.5575	- 1337.2877

Lead (Pb)

T^{0}C	K_0 (m^{-2}s^{-1})	ΔG^0 (KJ/mol)
30	1.0859	-207.6119
60	1.6337	-1359.0169
90	1.9446	-2007.2395

Nickel (Ni)

T ^{0}C	K_0 (m^{-2}s^{-1})	ΔG^0 (KJ/mol)
30	0.4899	1797.6437
60	0.7662	737.3424
90	1.1594	-446.3923

Zinc (Zn)

T^{0}C	K_0 (m^{-2}s^{-1})	ΔG^0 (KJ/mol)
30	0.5015	1738.6867
60	0.6173	1335.6290
90	0.8265	575.1246

4.0 CONCLUSION

Removal of heavy metals from industrial wastewaters can be accomplished through various treatment options, including such unit operations as chemical precipitation, coagulation, activated carbon adsorption, ion exchange, solvent extraction, foam flotation, electro-deposition, cementation, and membrane operations (Gunatilake, 2015).

Adsorbent from Sugarcane bagasse proves effective in removing heavy metal ions from water through adsorption. The petrochemical effluent wastewater contains six heavy metals, namely: Fe, Cd, Cu, Pb, Ni and Zn in the concentrations (mg/l) 0.7821, 0.0295, 0.0227, 0.0355, 0.3706 and 0.9780 respectively. The

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

effluent wastewater is alkaline with pH of 9.62 (Mohamed *et al*., 2017). The adsorbent contains three main functional groups at the surface, they are OH (alcohols), carbonyl (C=O) group and OH (acids). The results gotten from the experiment conducted revealed that the adsorption process of the heavy metals ions is dependent on contact time, adsorbent dosage and the solution temperature. Sugarcane bagasse is inexpensive natural waste and readily available, thus this study provides a low-cost effective means for removing metal ions from petrochemical effluent wastewater (Mohamed *et al*, 2017). Sugarcane bagasse has proven ability to adsorb metals without chemical modification to the adsorbent and its sorption was fitted well for Langmuir model with correlation factor R^2= 0.99 and separation factors R_l = 0.762 for Fe, 0.986, 0.971, 0.855, 1.000 and 1.000 for Pb, Ni, Zn, Cd and Cu respectively. R_l values of between $0< R_l<1$ represents a standard case of adsorption when adsorption occurs normally Ezzat *et al* (2010). Hence, the adsorption is favourable for Fe, Zn, Ni, and Pb and linear for Cd and Cu. Separation factor R_l = 0.762 corresponds to fast kinetics obeying pseudo-second order type. This result is similar to the value obtained for Fe (r^2 = 0.985) as the equilibrium data fitted well for Langmuir model when Ezzat *et al* (2010) carried out adsorption of metals on biosorbent. The ability of the adsorbent to remove the metal ions from the effluent wastewater is in the order $Fe > Ni > Cu > Pb > Zn > Cd$. The values of separation factor R_l for the various metal irons are approximately 1 suggesting linear and conformed to those typical of adsorbent from literature (Mohamed *et al*, 2017). The isotherm equilibrium studies fitted well for Langmuir model than Freundlich model for adsorption of the metals ions using adsorbent from sugarcane bagasse.

REFERENCES

Agency for Toxic substances and Disease Registry/Division of Toxicology and Environmental medicine (2006). Archived from the original.

Ahsan, H. (2007). Removal of Copper from Aqueous Solution using Orange Peel, Sawdust and Bagasse. . *Journal of Environmental Chemistry.8* (2), 21-25.

Baba, H, T Suneyama & K, Yazaki (2013). The Liver in Itai-Itai disease (chroni cadmium poisoning); pathological features and metallothionein expression. 26(9), 1228-1234.

Demirbas, O., Alkan, M. & Dorgan, M. (2002). The Removal of Victoria Blue from Aqueous Solution by Adsorption on a Low- Cost Adsorbent Material. *Springer Link Journal*. *8(4), 342-345.*

Center for Diseases Control and Prevention (2016, October 25). Lead poisoning investigation in Northern Nigeria.

Ezzat, M. S, Salwa, A. A. & Aliaa, A. F. (2010). Reactivity of Sugarcane Bagasse as a Natural Solid Phase Extractor for Selective Removal of Fe (111) and Heavy Metal ions from Natural Water Samples. *Arabian Journal of Chemistry. 1(4), 63-70.*

Freundlich, H. (1906). Adsorption in Solutions, Physical Chemistry. (57): 134.

Gunatilake, I.C. (2015). Methods of Removing Heavy Metals from Industrial Waste Water. *Journal of Multidiscipline Engineering Science*. 1(1), 1-13.

Horsfall, M. J., Abia, A. A. & Spiff, A. I. (2006). Kinetic Studies on the Adsorption of Cd^{2+}, Cu^{2+} and Zn^{2+} Ions from Aqueous Solutions by Cassava (Manihotesculenta) Tuber Bark Waste. *Journal Bioresource Technology*, 97(35), 283-291.

National Institute for Occupational Safety and Health. (2015, September 30). Effect of Heavy Metals on Human Health.

Journal of Newviews in Engineering and Technology (JNET)
Volume 4, Issue 3, December 2022
Available online at http://www.rsujnet.org/index.php/publications/2022-edition
e- ISSN: 2795-2215

Issabaye, G., Arroua, M.K & Sulaiman, N. M. (2006). Removal of Lead from Aqueous Solution on Palm shell Activated Carbon. *Bioresour. Technol 97*.

Lide, D.R. (2004). Handbook of chemistry and Physics. 8th ed. Boca Raton (FL): CR press. ISNB.

Moonis, A. & Rifaqat, A. (2008). Heavy metal pollution and its control through non-conventional adsorbents. *International Journal of Environmental Application and Science*. 3(2), 101-138.

Mohamed, H.. & Amaal, M.A. (2017). Removal of Some Heavy Metals from Aqueous Solutions Using Natural Wastes Orange Peel Activated Carbon. *IJRDO-Journal of Applied Science*. 3(3), 13-18.

Monisha Jaishanker, Tenzin Tseten, Naresh Anbalagan, Blessy B. Mathew & Krishnamurthy N. Beeregwoda. (2014). Toxicity, Mechanism and Health Effects of Some Heavy Metals. 7(2), 60-72

Paul, B. T., Clement, G., Dawyne, J. S. & Anita, K. P. (2014). *Heavy Metals Toxicity and the Environment*. 101:133-164.

Robert, Treybal. (1985): Mass-transfer Operations. 3rd edition. McGraw-Hill Book Company, London.

Sparks, D.L. (2001). Sorption and Release of Heavy Metals in Soil. Encyclopedia of Soils in the Environment. 53-237.

Yu Liu (2009). Is the Free Energy Change of Adsorption Correctly Calculated? *Journal of Chemical and Engineering Data. 54(7), 1980-1985.*

Zulkali, M. M. D., Ahmad, A. L., Norulakmal, N. H. & Ovyza, S. L. (2006). Husk as Heavy Metal Adsorbent Optimization with Head as Model Solution. *Journal of Bioresource Technology*, 97(13), 21-25.