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ECO-FRIENDLY SOLUTION FOR HEAVY METALS POLLUTION: SUGARCANE BAGASSE ACTIVATED CARBON IN GOLD MINING WASTEWATER

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Abstract–Liquid waste discharge from process industries, when not properly handled and disposed, poses a great risk to both man and the environment. Sugar cane bagasse was chosen as an activated carbon for this study. Two sugarcane bagasse-based adsorbents were prepared and used in batch experiments, Sugarcane Bagasse Ash (SBA) was obtained by subjecting to calcination in a furnace at 600℃ while Activated Sugarcane Bagasse (ACTSB) was prepared by soaking calcinated sugarcane bagasse in 1M HCl for 24 hours. The focus of this study is the use of low-cost and efficient agro-waste material for removing Cadmium (Cd^{2+}), Iron (Fe^{2+}), Lead (Pb^{2+}), and Zinc (Zn^{2+}) ions from Gold Mining Wastewater (GMW). The produced samples were characterized using Fourier Transform Infrared Spectroscopy (FTIR) for functional components (ligands) and X-ray Diffraction (XRD) for mineral constituent. Atomic Absorption Spectrometer (AAS) was used to determine the initial concentration of heavy metals. The effect of the absorbent dosage at constant temperature of 27℃, contact time of 20 mins, and agitation speed of 50 rpm to determine the removal efficiency were calculated. FTIR for SBA ranged from 695.1 to 2290.4 while ACTSB was at 777.1 to 2974.3. XRD quarty mineral content of SBA was high compare to ACTSB with a higher Magnesite content. SBA was the best in removal of Cd^{2+} and Zn^{2+}. While ACTSB was best in removing Fe^{2+}, and Pb^{2+} ions both at 0.6g dosage.

Keywords: Gold Mining Wastewater, Sugarcane Bagasse, Heavy Metals, Hydrochloric Acid.

1. Introduction

The sugar industry produces about 800 million tons of sugar annually on global scale which results in about 240 million tons of bagasse, some of which is used as fuel for mill boilers and electricity generation (Kalderis *et al.*, 2008). The unused bagasse is not readily biodegradable for composting and application in the farms and therefore, poses disposal problems for mill owners. Many efforts have been directed towards finding commercially viable applications of sugarcane bagasse (Osinubi and Alhassan, 2007; Aigbodion, 2008). For instance, it has been applied in the manufacture of pulp and paper products, charcoal and building materials (Botha and Blottnitz, 2006)

Bagasse is rich in lignocellulose and has abundant pores giving it a large internal surface area (Mahamadi, 2011). Due to this property, sugarcane bagasse has also been applied in removing some heavy metal ions from contaminated water. The degree of success in removing these ions from water differs from one metal to another, and depends on prevailing experimental conditions such as temperature, concentration and contact time (Gupta and Sharma, 2003; Ibrahim *et al.,* 2006; Batnagar and Mika, 2010).

Water contamination is a worldwide challenge that is caused by dyes, pathogens, turbidity, oil and its derivatives and heavy metals from industries and agricultural effluents (Estévez *et al.,* 2012). Heavy metals in particular persist in the environment indefinitely and cause dangers to public health, with lead, iron and cadmium being the most common heavy metals and with high toxicity (Mudhoo *et al.*, 2012). Lead poisoning causes low intelligent quotient, concentration disorders and behavioral changes in children. It causes degeneration of the axon, cerebral oedema, infertility, menstrual disorders, abortions and stillbirths in adults (Dahl *et al.,* 2014). Prolonged exposure to cadmium ions causes damage to kidneys, lungs, liver and it is carcinogenic (Fu and Wang, 2011).

The methods currently applied in water purification include chlorination to kill pathogens, electrochemical methods, membrane processes, reverse osmosis, chemical precipitation, biological processes, ion exchange and ion flotation to remove heavy metals (Batnagar and Mika, 2010). Some of these methods, however, generate toxic sludge that needs disposal and are relatively expensive. Adsorption is one of the alternatives for purification of water and wastewater before disposal. The most popular adsorbent used in wastewater treatment is the coal-based activated carbon but it is relatively expensive especially for small scale application (Sandhya and Tonni, 2003; Batnagar and Mika, 2010). There is increasing research interest in use of alternative adsorbents of lower cost obtained from locally available materials and wastes that are environment friendly (Wasewar, 2010). For example, agricultural wastes such as bagasse, banana and orange peels, rice and coffee husks, maize cobs and others can be effectively used in cleaning wastewater before disposal and in water treatment plants while curbing disposal challenges simultaneously (Batnagar and Mika, 2010). This study aim is to examine the possibility of removing heavy metals from wastewater using cost effective agricultural waste: sugarcane bagasse activated carbon with specific objectives which includes preparation of the adsorbent, characterization of the sugarcane bagasse and effect of adsorbent dosage for removal of heavy metals.

1.1 Study Area

ITAGUNMODI is located in Atakunmosa West Local Government Area of Osun State, Nigeria. It is situated approximately 45 kilometers northwest of Osogbo. The area is located within the Ilesha (Figure 1) schist Belt in Southwestern Nigeria between latitude 7025'043" and 7045'032" North of the Equator, and longitude 4035'023" and 4055'045" East of the Greenwich meridian (Asubiojo *et al.*, 2022). Quartz schist, quartzite, amphibolites, granite gneiss, amphibolites schist and migmatite gneiss complex are the major lithology unit in the study areas as described by (Asubiojo *et al.*, 2022). Their economy is primarily driven by agriculture, artisanal mining, hunting and trading.

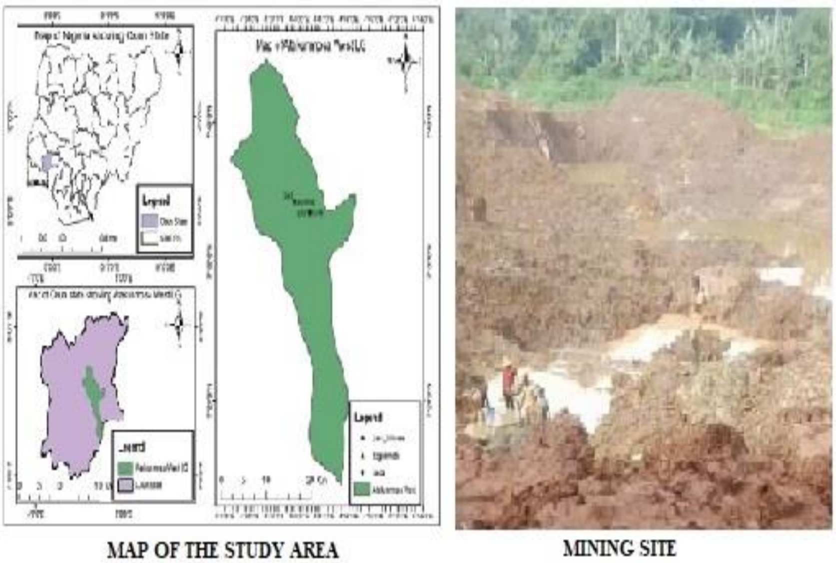

Figure 1: Study Area

2. Materials and Methods

Sugarcane bagasse obtained from Owode market around Offa town in Kwara state. Wastewater sourced from gold mining activities (Itagunmodi,Atakunmosa West, Osun State), Hydrochloric acid (HCl), Oven, mechanical grinder, sieve, and weighing balance are among the tools utilized. A beaker, conical flask, dropper, funnel, volumetric flask, thermometer, Whatman filter paper, and pH litmus paper are some of the apparatuses used.

2.2 Preparation of Sugarcane Bagasse

The sugarcane bagasse was washed with distilled water to remove dirt. It was sun dried for 24 hours in preparation for activated carbon. 600g of cleaned dry sugarcane bagasse was weigh and subjected to calcination in a furnace at 600°C. Transforming it into ash which produced 60g of ash that was allowed to cool and then packed in plastic bottles for further experiment.

Activated Sugarcane Bagasse (ACTSB).

40g of sugarcane bagasse ash was activated by soaking in a solution 1M HCL for 24 hours. It was then thoroughly washed in distilled water and sun-dried for 24 hours. The material obtained was used in the adsorption experiments as sugarcane bagasse activated (SBACT).

Figure 2: Activated Sugarcane Bagasse (ACTSB)

2.3. Characterization of sugarcane bagasse

The produced sugarcane bagasse was characterized for ligands (functional components), and minerals Constituents.

2.3.1. Fourier Transform Infrared Spectrometer (FTIR)

Fourier Transform Infrared Spectrometer is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid, or gas. An FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range, this confers a significant advantage over a dispersive spectrometer, which measures intensity over a narrow range of wavelengths at a time. The diamond crystal was cleaned with methanol and allowed to dry, then cleaned with dry tissue paper. The sample was placed on the crystal surface and a spectrum was generated by the machine at a wavelength between 400 and 4000 cm-1 which provide details on the surface ligands of the sugarcane bagasse.

2.3.2. Constituents of minerals X-ray Diffraction (XRD)

Analysis was used to assess the mineral constituents. Powdered samples were pelletized and sieved to 0.074mm. These were later taken in an aluminum alloy grid (35mm x 50mm) on a flat glass plate and covered with a paper. Wearing hand gloves, the samples were compacted by gently pressing them with the hand. Each sample was run through the Rigaku D/Max-lllC X-ray diffractometer developed by the Rigaku Int. Corp. Tokyo, Japan and set to produce diffractions at scanning rate of 2^0/min in the 2 to 50^0 at room temperature with a CuKa radiation set at 40kV and 20mA. The diffraction data (d value and relative intensity) obtained was compared to that of the standard data of minerals from the mineral powder diffraction file, ICDD which contained and includes the standard data of more than 3000 minerals.

2.3.3 Analysis of concentrations of metals present in the gold mining wastewater

Initial concentrations of the metals (Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+}) present in the wastewater before treatment were estimated using AAS analysis at Chemical department of ABUAD, Nigeria. The digested wastewater was sucked by the compressor on the main machine and it later sent signal to the computer. The equipment was adjusted in each time to the wavelengths of metals to be analyzed while its monochromator measured the quantities of the absorbed metals. The flame that was in the analysis is air-acetylene. The temperature formed in the air-acetylene flame was around 2300 ˚C (Adetoro *et al*., 2022).

2.3.4 Adsorption experiment for removal of heavy metals

The impact of varying adsorbent dosages on the adsorption of lead, iron, cadmium, and zinc was investigated through a series of adsorption experiments. Different adsorbent doses of Sugarcane Bagasse Ash (SBA) and Activated Sugarcane Bagasse (ACTSB), ranging from 0.1g to 0.6g, were employed in these experiments, quantified using weighing balance, conducted at a standard room temperature of 27℃. To initiate the experiments, precisely measured doses of adsorbent were added to 100mL of wastewater, quantified using a beaker. The mixture was then transferred to a conical flask for agitation, maintaining a constant speed of 50 Revolutions per Minutes (rpm) for a duration of 20 minutes. Subsequently, the mixture underwent filtration using Whatman filter paper No. 110, and the residual concentrations of Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} were determined using AAS machine.

The removal efficiency (%) of each heavy metal was calculated by the following equation:

$$Percentage\ removal = \frac{c_i - c_f}{c_i} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad (1)$$

Where C_i and C_f are initial and equilibrium concentrations of heavy metals respectively (Adetoro *et al*., 2022).

3. Results and Discussion

3.1 Surface Chemistry

Fourier Transform Infrared Spectroscopy (FT-IR) spectra of the adsorbents (Figure 3) were obtained to determine the functional groups formed which may be responsible for the attachment of the lead, iron, cadmium and zinc ions. The FTIR spectra of SBA and ACTSB were used to determine the vibrational frequency changes of the functional groups in the adsorbents. The spectra of ad sorbents were measured within the range of 650–4000 cm^{-1} wave numbers. The spectra were plotted using the same scale on the transmittance axis for all the adsorbents.

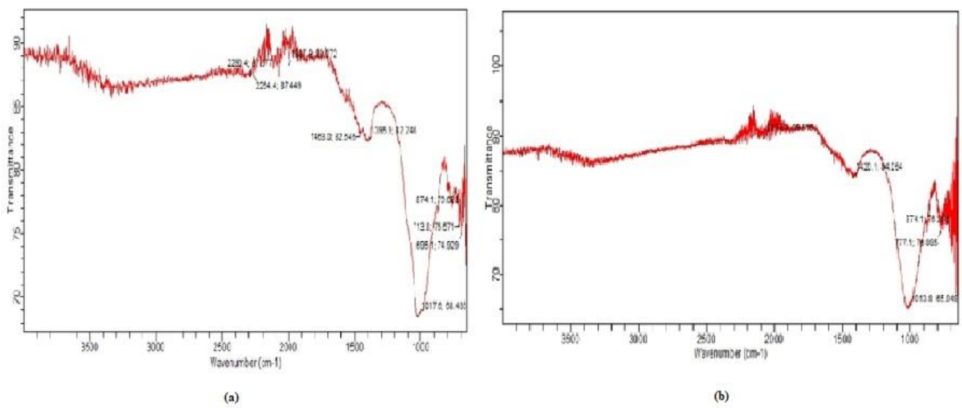

Figure 3: (a and b): FT-IR Spectra of SBA and ACTSB

Table 1: Wavenumbers and chemical groups of FT-IR absorption bands for both SBA and ACTSB

S/N	SBA	ACTSB		Functional group	Appearance (Intensity)	Compound class
1	2290.4		disappear	O=C=O stretching	strong	carbon dioxide
2	2264.4		disappear	N=C=O stretching	strong broad	isocyanate
3		2074.3	appear	N=C=S stretching	strong	isothiocyanate
4	1997.9		disappear	C=C=C stretching	medium	allene

5	1463.1	1420.1	stretching downward	C-H bending	medium	alkane
6	1395.9		disappear	O-H bending	medium	carboxylic acid
7	1017.6	1013.8	stretching downward	C-F stretching	strong	fluoro compound
8	874.1	874.1	no stretching	C-H Bending	strong	1,3-disubstituted
9		777.1	appear	C-H Bending	strong	1,2,3-trisubstituted
10	713.8		disappear	C=C bending	strong	alkene
11	695.1		disappear	C=C bending	strong	alkene

The above table shows the wavenumber range, functional group assignment, intensity (weak, medium, strong) and possible compound class for various peaks in the FTIR spectra of SBA and ACTSB. Several peaks disappear in ACTSB compared to SBA, indicating the removal of certain functional groups during HCL activation. The peaks at 2290.4 cm^{-1} (assigned to C=O stretching in carboxylic acids) and 1395.9 cm^{-1} (assigned to O=H bending) are absent in ACTSB. Appearance of new peaks was shown in ACTSB, such as the peak at 777.1 cm^{-1} (assigned to C-H bending in 1,2,3-trisubstituted alkenes). Furthermore, the intensity of some peak changes between SBA and ACTSB, such as the peak at 1463.1 cm^{-1} (assigned to C-H bending in alkanes) is weaker in ACTSB compared to SBA. These observations suggest that HCl activation changes the surface chemistry of sugarcane bagasse by removing certain functional groups and introducing new ones, which may possibly influence adsorption capacity, chemical reactivity and overall treatment performance.

3.2 Mineralogical Composition

The two graph below is an XRD pattern of SBA and ACTSB (Figure 4). The peaks in the graph correspond to the different minerals present. The 2Theta angle is the angle at which the X-rays are diffracted by atoms in the mineral. The main minerals present in sugarcane bagasse are silica (SiO_2), potassium oxide (K_2O), calcium oxide (CaO), and magnesium oxide (MgO) (Ajayi et al., 2000).

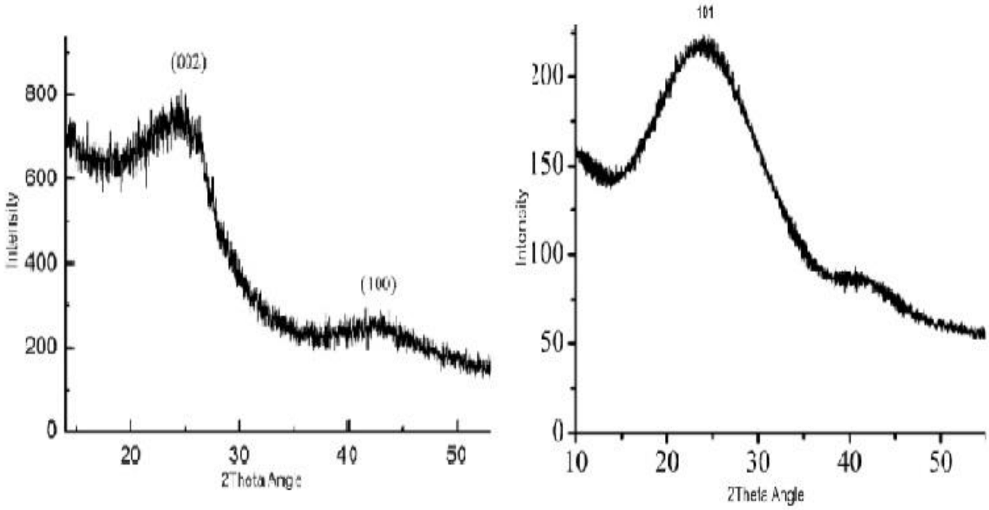

Figure 4: XRD of SBA and ACTSB

The result of SBA has two different peaks correspond to the two different minerals present in the sample. The sharp peak at around 25° 2Theta corresponds to quartz, which is a form of silicon dioxide (SiO_2). The small peak at around 42° 2Theta corresponds to magnesite, which is magnesium carbonate

($MgCO_3$), The sharp peak of quartz shows its abundance in the sample of SBA. Also in the ACTSB, the smaller peak at around 26° 2Theta corresponds to quartz, which is a form of silicon dioxide (SiO_2). The small peak at around 43° 2Theta corresponds to magnesite, which is magnesium carbonate ($MgCO_3$), which implies that ACTSB mainly composed of quartz, with smaller amount of magnesite. The relative intensity of the peaks in the graph shows that the relative intensity of the ACTSB is lower than the SBA. The HCl activation affect the abundance of different minerals in sugarcane bagasse by reducing their relative abundance present in the ordinary bagasse ash, which can lead to potential changes in its effectiveness for treating wastewater.

3.3 Effect of Adsorbent Dosage

The adsorption capacity of the adsorbent was investigated by varying the adsorbents dosage from 0.1g to 0.6g exposing each dose to 100 mL of Gold Mining Wastewater (GMW) solution Cd^{2+}, Fe^{2+}, Pb^{2+} and Zn^{2+} at 50 rpm, at 20 mins, and 27 ℃ room temperature. The initial treatment of the GMW shows that Fe^{2+} has a highest concentration which is above the WHO standard, followed by Cd^{2+}, Pb^{2+} and Zn^{2+}.

Table 2: Initial concentration of heavy metals

Heavy metals	Before Treatment	W.H.O (2021)
Cd^{2+}	10.036	0.003
Fe^{2+}	10.174	1
Pb^{2+}	6.082	0.01
Zn^{2+}	3.381	5

The adsorptive capacity and percentage removal of each adsorbent towards the selected heavy metals were calculated. Cd^{2+} has the highest percentage removal with SBA which is 99.15%, and Lead has the highest percentage removal using Activated Sugarcane bagasse (SBACT) which is 98.50%.

Table 3: Removal Efficiency of SBA

Dosage (g)	REMOVAL EFFICIENCY OF HEAVY METALS			
	Cd^{2+}	Fe^{2+}	Pb^{2+}	Zn^{2+}
0.1	95.51	94.08	94.61	81.25
0.2	95.83	94.44	94.85	84.24
0.3	97.27	94.68	96.94	89.41
0.4	97.3	94.78	97.71	91.81
0.5	98.68	95.32	97.98	96.18
0.6	99.13	96.65	98.22	96.36

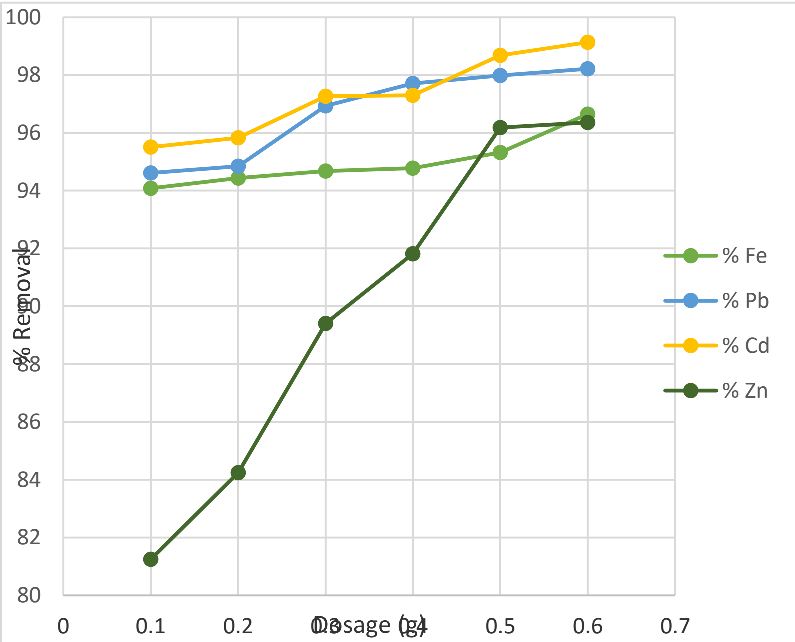

Figure 5: Percentage removal SBA

Table 4: Removal Efficiency ACTSB

Dosage (g)	REMOVAL EFFICIENCY OF HEAVY METALS			
	Cd^{2+}	Fe^{2+}	Pb^{2+}	Zn^{2+}
0.1	92.28	96.39	93.82	80.07
0.2	96.04	96.75	95.64	84.41
0.3	96.12	97.28	96.42	91.6
0.4	96.57	97.81	96.68	93.58
0.5	96.88	98.08	97.19	94.79
0.6	97.32	98.35	98.5	96.27

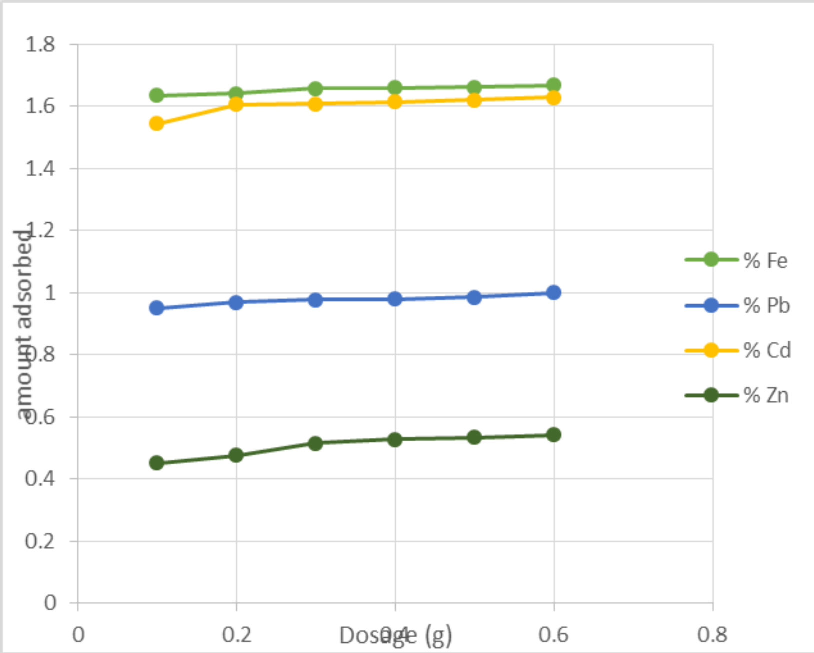

Figure 6: Percentage removal of ACTSB

The results show that as the adsorbent doses were increased, the percentage removal of all the metal ions present in the wastewater increased for both the two adsorbents (SBA and ACTSB).

SBA was the best in removal of Cd^{2+} and Zn^{2+}. With Cd^{2+} at 99.13% using 0.6g of SBA with a difference of 1.81% to ACTSB which is 97.32%, and Zn at 96.36% with a difference of 0.09% to ACTSB whose removal percentage is 96.27%. While, ACTSB was the best in removal of the other two metal ions which are Fe^{2+}, and Pb^{2+} ions. With Fe^{2+} at 98.35% with a difference of 1.70% to SBA whose removal percentage is 96.65%, and Pb^{2+} at 98.50% with a difference of 0.28% to SBA whose removal percentage removal is 98.22% using dosage of 0.6g.

4. Conclusion

The following conclusions were drawn from the study:

i. The investigation into the dosage of Sugarcane bagasse ash (ASB) and Activated sugarcane bagasse (SBACT) adsorbents in Iron Fe^{2+}Lead Pb^{2+}), Cadmium $Cd^{2+}$and Zinc (Zn^{2+}) removal from gold wastewater revealed significant insights into the efficacy of varying dosages of ASB and SBACT in removing Fe^{2+}, Pb^{2+}, Cd, and Zn^{2+}. Experimental results indicate a positive relationship between dosage and metal removal efficiency, with a dosage of 0.6g showcasing promising results throughout the study.

ii. Sugarcane bagasse ash was the best in removal of Cd^{2+} and (Zn^{2+}). With Cd^{2+} at 99.13% using 0.6g of sugarcane bagasse ash with a difference of 1.81% to activated sugarcane bagasse which is 97.32%, and Zn^{2+} at 96.36% with a difference of 0.09% to activated sugarcane bagasse whose removal efficiency is 96.27%. While, activated sugarcane bagasse was the best in removal of the other two metal ions which are Fe^{2+}, and Pb^{2+} ions. With Fe^{2+} at 98.35% with a difference of 1.70% to ASB whose removal efficiency is 96.65%, and Pb^{2+} at 98.50% with a difference of 0.28% to ASB whose removal efficiency is 98.22%. It is evident that sugarcane bagasse adsorbents can effectively remove Fe^{2+}, Pb^{2+} Cd^{2+} and Zn^{2+} from GMW at 20 mins contact time, normal room temperature of 27℃ and agitation speed of 50rpm using 0.6g adsorbent.

iii. The use of sugarcane bagasse as a natural adsorbent is not only proficiency eliminate Fe^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} from GMW but also present an eco-friendly approach to wastewater treatment. This renewable and cost-effective material exhibits substantial potential to mitigate the environmental impact of heavy metals in wastewater. Additionally, this project research highlighted the importance of dosage optimization when using SBA and ACTSB for metal ions removal.

iv. Conclusively, the increased dosage of sugarcane bagasse demonstrated notable improvements in Fe^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} removal from GMW, thereby providing potential solutions to environmental problems associated with industrial wastewater treatment.

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