Adsorption and Desorption Efficiency of a Sugarcane Bagasse in the Removal of Fe$^{2+}$ from a Galvanizing Industry

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Abstract: Disposal of industrial effluent is of health concern. Especially effluent from industries such as metal galvanizing, tannery, metallurgical, mining, chemical, battery and nuclear, agriculture, and others that generate heavy metals which deteriorate soil, groundwater quality and bio accumulate in food chains these are particularly harmful to both plants and animals. Removing Heavy Metals are mostly expensive, this necessitate researches on the efficient and effective use of agro based low cost adsorbent, which is also an efficient form of agricultural waste disposal. This study is to remove Fe$^{2+}$ ions in industrial wastewater using raw Sugarcane Bagasse (SCB) adsorbent. The initial concentration of Fe$^{2+}$ ions in the industrial (galvanizing) wastewater was first analyzed to determine the removal efficiency of SCB in adsorbing Fe$^{2+}$ from wastewater and the optimum conditions (such as effect of phase contact time, rotating speed and concentration dosage) of the adsorbent was determined. The following characteristics of the agro waste material and wastewater were determined; Fourier Transform Infrared Spectroscopy FTIR analysis, digestion of wastewater samples and Atomic Absorption spectrophotometry (AAS) analysis. The results show that percentage removal of Fe$^{2+}$ ions from aqueous solution was 95.11% with the raw sugarcane bagasse adsorbent. The sorption capacity decreases with increasing dosage concentration and phase contact time and the desorption studies demonstrated important data for the regeneration and recovery of both adsorbent and heavy metal ions.

Keywords: bagasse; adsorption; desorption; heavy metal.

1. Introduction

The use of water resources in the world today is posing a serious environmental challenge [1], the solution to a great extent lies in treatment of wastewater that originates from anthropogenic exercises in different industries: for example, metal galvanizing, metallurgical, mining, chemical, tannery, battery and nuclear, agriculture, and others.

Heavy metal is one of the most biologically dangerous and toxic components of an industrial effluent and this is important to be controlled [2-4]. Over the past decades, there is an increase in the flow of metallic substance in the aqueous environment, which is caused, by a significant increase in the use of heavy metals. This increased heavy metal pollution is of great concern. Because of their high toxicity for human health, heavy metal concentration in wastewater is entirely limited by high standard [5].

Iron is a persistent heavy metal, which is toxic and bio-accumulative [6]. It is not decomposable, not easily metabolizes and hazardous to human health. The different potential sources of iron pollution are metallurgical and metal finishing (galvanizing), copper plating and pickling, primer paints, fungicides, corrosion inhibitors in cooling and boiler systems [7]. Overabundance body iron can be exceptionally toxic. This toxicity involves many parts of the body, lead to a variety of critical conditions, such as lung, liver and heart disease. Others include diabetes mellitus, immunodeficiency and hormonal abnormalities. Free–radical reaction of iron is believed to principally caused iron over-
burden, which caused tissue damage. The diseases related with iron overload can be effectively managed or forestalled. Along these lines, there is a requirement for dire consideration regarding remediate industrial wastewater, which is one of the major sources of Fe$^{2+}$ ion causing environmental problem.

Agricultural wastes are low cost adsorbents, which can be a reasonable alternative to activated carbon in the treatment of heavy metal contaminated wastewater. Sugarcane bagasse (SCB) is a by-product of agricultural wastes, which can be used, in the natural form as well as in a modified form. It consists of lignin (23%), polyoses (27%) and cellulose (50%). It is obtained from the fibrous material left after cane stalk pulverizing and juice extraction [8]. Sugarcane bagasse activated carbons (SBACs) have a well-developed porous structure (large mesopores and micropore volumes) and a high specific surface area, as well as different surface functional groups (including carboxyl, carbonyl, phenol, quinone, lactone, and others) bound to the edges of the graphite-like layers, which make them a heavy metal contaminant removal [9].

Its biological component polymers, makes SCB riche in phenolic and hydroxyl groups. These group increases its adsorption capacity when they are chemically altered [8,10]. Examples of chemical used for the modification of sugarcane bagasse include sulphuric acid, succinic anhydride, pyromellitic anhydride, citric acid, sodium bicarbonate, ethylenediamine, etc. These acids are particularly used as activating agents, which polymerized with SCB to increases the number of chelating sites and pore spaces (porosity) for effective heavy metal removal from wastewater [8].

This study is to remove and recover Fe$^{2+}$ ions in industrial wastewater using raw sugarcane bagasse adsorbent and the removal efficiency in adsorbing Fe$^{2+}$ from wastewater

2. Materials and methods

The preliminary experiment study was conducted on the wastewater samples collected from Nigeria Machine Tools (NMT), Kilometer 8, Ikirun Road Osogbo, Osun State, Nigeria. The sample was collected from Coating Department (Electroplating Plant) of the company. Sugarcane (SC) stem was collected from Ladoke Akintola University of Technology Research farm, sugarcane juice of the (SC) stem collected from research farm was extracted by a pestle and mortar after peeling. The sugarcane bagasse (SCB) was rinsed inside distilled water to remove ligneous completely, cellulose and trapped impurities in the bagasse. The filtration process was repeated and the final clean bagasse was collected in a stainless pan for oven dry. SCB was then oven dry for 24hrs at 40°C after which it was grinded. The SCB powder obtained was graded in sieve No. 200 and the fines passing through the sieve were stored in airtight 0.75L PET bottles [11]. The following characteristics of the agro waste material and wastewater was determined; FTIR analysis, digestion of wastewater samples and Atomic Absorption spectrophotometry (AAS) analysis.

Fourier Transform Infrared analysis was carried out on the grinded agro waste sample (SCB) using Infrared Spectrophotometer model: BUCK M530 series to determine its functional group in order to evaluate its rate of absorption. Atomic Absorption Spectrophotometry (AAS) analysis was carried out to determined the concentration of the untreated wastewater, the final concentration after treatment and the control sample. The instrument used is the atomic absorption spectrophotometer (AAS) with model number PG6990

2.1. Adsorption Batch Experiment

The batch experiments with One Factor at A Time (OFAT) were conducted on the wastewater samples varying the factors of adsorbent dosage, contact time and rotating speed of rotary incubator.

i. Adsorption Study: This was carried out with 50ml of wastewater sample poured into 250ml conical flask and 0.2g of prepared SCB adsorbent was added, placed on a rotary shaker at 150 revolutions per minute (rpm) at room temperature for one hour. The suspension was filtered and the filtrate was subjected to AAS analysis.

ii. Effect of Adsorbent Dosage: this was studied with the varying dosages of 0.2, 0.4, 0.6, 0.8, 1.0g into 50ml of the wastewater sample in a conical flask respectively and agitated at 150 rpm for 60mins and the suspension was filtered and the filtrate was subjected to AAS analysis.
iii. **Effect of Contact Time**: This was performed as 0.2g of adsorbent was added to 50ml of wastewater samples in different conical flasks, placed on a rotary shaker and agitated at 150 rpm for each of the different contact times chosen as 20, 40, 60, 80 and 100mins respectively.

iv. **Effect of Rotating Speed**: 0.2g of the adsorbent was measured into 50ml of wastewater sample into different conical flasks and subjected to various agitation rpm from 50 to 200 at 50 rpm intervals. The filtrate from each batch was then subjected to AAS analysis

### 2.2. Desorption Study

Desorption of metal ions from the adsorbents was carried out by washing loaded sorbents (initial concentration of iron, 10.871 mg/L, dosage 0.2g, shaking speed 150 rpm, at room temperature) with 20ml of HCl eluents in a glass petri dish at varied concentrations of 0.1M and 0.3M. This is in accordance with the report of [12]. Although, different desorbing agents such as; H₂SO₄, and HNO₃ at different concentration can also be used for desorption of loaded sorbent. The phase contact time in the range 300 – 360mins was applied to determine the time at which the highest percentage of desorption (D%) can be achieved. In this study, the metal concentration was determined in the samples removed after 360mins. As acids concentration increases, desorption efficiency also increases. However, higher acid concentration may damage the structure of the adsorbent or reduce the adsorption and desorption efficiency of the adsorbent

### 2.3. Centrifugation

After the desorption study, the solution was subjected to centrifugation process in order to separate the desorbed metals ions from the adsorbent. The solution was poured into a test tube and loaded inside the centrifuge machine test tube hanger; the machine was powered, and set at 1500 revolutions per minute for 30minutes. The acid filtrate was decanted, left only pure metals ion and adsorbent at the bottom test tube, which was picked by scoop and oven dried for Scanning Electron Microscope (SEM) analysis

### 3. Results and discussion

The following are the results gotten;

#### 3.1. Heavy metals concentration of the sample before treatment

Table 1. shows the concentration of heavy metals present in the effluent from the electroplating department of Nigeria Machine Tools, Osogbo, Osun State Nigeria.

#### 3.2.

| Metals          | WHO Standards MPL | Nigeria Standard MPL | Present Study Mg/l |
|-----------------|------------------|----------------------|--------------------|
| Cadmium (Cd)    | 0.005mg/l        | 0.003mg/l            | ND<sup>b</sup>     |
| Manganese (Mn)  | 0.50mg/l         | 0.20mg/l             | 0.185mg/l          |
| Lead (Pb)       | 0.015mg/l        | 0.01mg/l             | 0.079mg/l          |
| Zinc (Zn)       | 5.00mg/l         | 3.0mg/l              | 31.859mg/l         |
| Iron (Fe)       | 0.30mg/l         | 0.30mg/l             | 10.848mg/l         |
| Chromium (Cr)   | 0.05mg/l         | 0.05mg/l             | 0.270mg/l          |
| Cobalt (Co)     |                  | 0.05mg/l             | 0.403mg/l          |
| Copper (Cu)     | 1.00mg/l         | 1.00mg/l             | 0.328mg/l          |

<sup>a</sup>Maximum Permissible/Permitted Levels  
<sup>b</sup>Analyzed for but not detected/value is below reportable limits  
<sup>c</sup>Blank cells indicate that no, citable information was available.
Eight heavy metals were analyzed for in the wastewater, the results revealed that seven metals were presents which are Manganese (Mn), Lead (Pb), Zinc (Zn), Iron (Fe), Chromium (Cr), Cobalt (Co) and Copper (Cu). Only Cadmium (Cd) was not present in the effluents. The table shown that Zinc (Zn) has the highest value of 31.859mg/l, which implies that the zinc has the highest percentage of metals used in the electroplating process taking place in the department, followed by Iron (Fe) with 10.848mg/l values, followed by Cobalt and Lead (Pb) has the lowest value of 0.079mg/l. Figure 1. shows these metals concentration in the percentage. Only copper concentration with 0.328mg/l value is less than WHO and Nigerian standards.

![Figure 1. Metals concentration in percentage in the wastewater prior to treatment.](image)

3.3. Fourier transform infrared spectroscopy (FTIR) spectrum interpretation

Transform Infrared Spectroscopy FTIR was used to determine the surface functional groups of Sugarcane Bagasse. FTIR was carried out using Infrared Spectrophotometer model: BUCK M530 series. Infrared spectroscopy is a powerful tool for identifying the presences of functionalities such as Hydroxyl, Carbonyl, alkane, aromatic compounds and amino compounds etc. the vibrational spectrum of a molecule is considered a unique physical property and is characteristics of the molecule. The most useful region of the infrared radiation extends from above 2.5 to 16 microns. An infrared Spectrum is usually presented in a plot of the percentage of radiation of each wavelength transmitted through the sample (0% transmission corresponds to total absorption by the sample) [13].

There are two molecular vibrations viz:

i. Stretching Vibration which changes distances between adjacent atoms, and

ii. Bending vibration which change bond angles

Note: Bending vibration requires less energetic photons than do stretching vibration. Therefore, they occur at lower frequencies (lower wavenumber).

Infrared spectrum is generally divided into four (4) regions or categories namely;

i. $4000 – 2500 \text{ cm}^{-1}$ ----- $\text{O – H, N – H, C – H}$ stretching,

ii. $2500 – 2000 \text{ cm}^{-1}$ ----- $\text{C = C, C = N}$ stretching

iii. $2000 – 1500 \text{ cm}^{-1}$ ----- $\text{C = C}$, stretching

iv. $1600 – 400 \text{ cm}^{-1}$ ----- Various bending vibrations or Fingerprint regions.
Figure 2. FTIR spectrum for SCB powder sample.

Figure 2. above shows band of 3314.5 (3300 – 3500cm⁻¹) due to N – H stretching bond, Amines or Amides functional group or class with medium intensity of absorption. The shoulders observed at 2889.7 (2850 - 2970cm⁻¹) due to C – H stretching bond, alkanes functional class and medium – strong intensity of absorptions. The band 1689.6 is due to C ≡ C stretching bond, Alkenes group and variable intensity of absorption and near 1450cm⁻¹ is due to aromatic rings with strong intensity of absorptions.

3.4. Adsorption Studies

Table 2. – Table 4. show the results of AAS analyses on the effect of the adsorbent dosage, rotating speed and contact time on the adsorbent in the studied adsorption batch experiment of the Fe²⁺ in the wastewater sample.

| Dosage (g) | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|-----------|-----|-----|-----|-----|-----|
| Iron (Fe)(ppm) | NDᵇ | ND | 0.003 | ND | ND |
| NDᵇ Analyzed for but not detected/value is below reportable limits |

| Speed (rpm) | 50 rpm | 100 rpm | 150 rpm | 200 rpm |
|-------------|--------|---------|---------|---------|
| Iron (Fe)(ppm) | 1.077 | 0.700 | 0.466 | 0.728 |
| (% removal) | 90.07 | 93.54 | 95.70 | 93.27 |

| Contact time | 20mins | 40mins | 60mins | 80mins | 100mins |
|--------------|--------|--------|--------|--------|---------|
| Iron (Fe)(ppm) | 0.374 | 0.371 | 1.349 | 1.994 | 0.863 |
| (% removal) | 96.55 | 96.58 | 87.56 | 81.62 | 94.04 |

SCB contains cellulose, hemi-cellulose and lignin which makes it show different efficiencies for the removal of Iron (Fe) at varied pH.
Figure 3. Percentage removal with adsorbent concentration.

Figure 4. Percentage removal with rotating speed of rotary incubator (rpm)

Figure 5. Percentage removal with contact time of the adsorbent.
3.5. Desorption Studies

(a)  
(b)  
(c)  
(d)  

Figure 6. a–6.d: SEM images of SCB sample before treatment at (a) 500x, (b) 1000x, (c) 1500x and (d) 2000x magnifications.

(a)  
(b)  
(c)  
(d)  

Figure 7a–7d: SEM images of loaded adsorbent after desorption process at (a) 500x, (b) 1000x, (c) 1500x and (d) 2000x magnifications.

In Figure 6a–6d and Figure 7a–7d respectively, the Scanning Electron Microscope (SEM) images of raw adsorbent before treatment and loaded adsorbent after desorption experiment at four different magnifications are presented. It can be proved or argued that raw adsorbent has a heterogeneous, well-developed structure. Furthermore, according to the SEM analysis, the sorbed heavy metal ions are uniformly distributed on the surface and interior pores of the SCB adsorbent and they are characterized by a smoother compact and uniform structure[4].

4. Conclusion

This research works shows that sugarcane bagasse is a good low cost, abundantly available and can be used as an effective biosorbent for removal of Fe$^{2+}$ ions in aqueous solution. The adsorption process is a function of the metal ion concentrations, contact time, rotating speed and adsorbent dosage. The maximum percentage removal of Fe$^{2+}$ ions from aqueous solution was found to be 95.11% with the raw sugarcane bagasse adsorbent. Sorption capacity reduces with the increasing dosage concentration and phase contact time. Desorption studies showed important data for the
regeneration and recovery of both adsorbent and heavy metal ions. Desorption of the sorbed adsorbent was characterized by SEM analysis; the images generated confirmed the recovery of the metal ions on the surface pores of the SCB adsorbent.

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