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Biosorption potentials of sawdust in removing zinc ions from aqueous solution

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Abstract:
Timber processing industries generate enormous waste, which constitutes environmental nuisance. However, the sawdust contains several organic compounds that could actively remove heavy metal ions from an aqueous solution through the adsorption process. This study investigated the efficacy of sawdust of *Albizia zygia and Gmelina arborea* in removing Zinc (II) under two factors affecting adsorption, Contact time and pH. Sawdust samples were sieved through a screen size of 2.0mm, after which a portion of sawdust for each species was subject to pre-treatment by boiling while the other parts were kept as control samples (untreated). The effect of pH on the removal efficiency of the biosorbent was determined by adding 0.2g of the sawdust (treated and untreated) into six conical flasks containing the metal solution (50ppm) at different pH values. There was a significant difference in the removal efficiency of both treated and untreated samples for both species. Removal efficiency also increased with time, with maximum Zn (II) biosorption achieved at 90 minutes. Removal efficiency increased with pH and reached optimum pH of 4. Both species' maximum Zn (II) biosorption (*Albizia zygia* = 17.22, *Gmelina arborea* = 17.92) compared favourably with other biosorbent used in previous studies. From this study and based on availability, cost-effectiveness, ability to be recovered and reused, sawdust of *Albizia zygia* and *Gmelina arborea* are proven alternative adsorbents treatment of water towards ensuring that quality water is available for humans, plants, and animals.

Keywords: Adsorption, Adsorbent, contaminated water, Sawdust, Zinc ion.

Introduction

Water pollution has become a severe challenge in our present world. The primary sources of freshwater pollution can be attributed to the discharge of untreated sanitary, toxic industrial wastes, dumping of industrial effluents, and runoff from agricultural fields[1,2]. These industrial and municipal wastewaters frequently contain heavy metal ions[3] such as lead, copper, cadmium, zinc, and nickel, which have been the most common pollutants found in industrial effluents[4]. Consumption of these heavy metals in drinking water has been hazardous to human health as it damages the liver and nerves and blocks functional groups of vital enzymes and bones[5].

Heavy metals have been identified as the most problematic micropollutants in water[6] because of their non-degradability and severe toxicity[7]. They also have the potential for long-term contamination even at a concentration below allowable limits due to their accumulative nature[8]. They can move throughout the food chain[9]. One of the heavy metals considered in this study is zinc, which commonly exists as Zn^{2+} in an aqueous solution. According to WHO[10], the permissible limit for Zn^{2+} in drinking water is 3.0 mg/L. However, high concentration can cause metal fume fever, restlessness, skin irritations, anaemia, and nausea[2]. A global sanitation report by WHO/UNICEF[11] revealed that “70 to 80% of all illnesses in developing countries are related to water contamination, particularly susceptible to children and women”[2].

The efficient removal of heavy metals from water and minimizing risk presents a new challenge for water managers and industries[12]. The conventional methods used to remove these heavy metals from water and wastewater include chemical precipitation, chemical oxidation/reduction, electrochemical treatment, filtration, evaporation recovery, reverse osmosis, ion-exchange, and electro-coagulation[13], which have become unsustainable. However, these methods also have significant disadvantages, which include incomplete removal, expensive, high-energy requirements, aggregation of metal residues, and production of toxic sludges[14,15]. Conversely, adsorption technology has emerged as an improved treatment technique[15,16], with a growing interest in developing practical and low-cost adsorbents for industrial application[2,5].

For decades, activated carbon has been a good candidate for adsorbing pollutants due to its porous structure with a surface area ranging from 600 to 2000 m^2/g[1], compared to other biosorbent materials[17]. However, its applications are limited because its production process is expensive, and it cannot regenerate quickly. It is, therefore, essential to note that cost is a crucial factor in selecting a suitable commercial adsorbent. An adsorbent is considered low-cost or cheap "if it is abundant in nature, requires little processing, and is a by-product of waste material from waste industry"[2].

Biosorption, which uses natural materials such as wastes from agricultural and industrial activities and microorganisms as an adsorbent in removing metal ions from an aqueous solution[2], has proven very useful and cost-effective commercial adsorbent for industrial application over the past two decades. This method has significant advantages: low operational cost, high efficiency, regeneration of biosorbent, and removal of contaminants even in low concentration, which is another major limitation for most conventional approaches[15].

Forest industries in Nigeria generate enormous waste materials. In 2010, sawmills in Nigeria generate over 1,000,000 m^3 of wood wastes while plywood mills generated about 5,000 m^3 of waste, most of which are disposed of poorly and consequently contribute to environmental degradation[18]. The sawdust from wood contains cellulose, hemicelluloses, lignin, ash, tannins, and other phenolic compounds (active ion-exchange compounds that could bind heavy metal ions)[19]; they are cheap and abundantly available. Investigating the potentials of sawdust generated from some of the most processed wood species in Nigeria as adsorbents in removing heavy metals from the contaminated water have become imperative. The use of sawdust as a viable biosorbent presents a novel approach in managing this abundant industrial by-product in an economical and environmental-friendly manner. Therefore, this study investigated the adsorbent potential of sawdust from two important wood species, *Albizia zygia* and *Gmelina arborea*, in removing Zn^{2+} from contaminated water.

Materials and method

The adsorbent used and preparation.

The sawdust collected was first screened through a sieve of screen size 2.0 mm, to obtain uniformly sized particles used for the adsorption tests in this study. The sieved sawdust was divided into two halves, with each weighing 75 grams. One-half of each species' divided portion was boiled for 1 hour, washed with clean water, and cooked for another 1 hour to effectively remove a large percentange of extractives present. The remaining was left untreated. The samples from the wood species (treated and untreated) were dried at 105^0C for 2 hours using an oven to remove moisture from the sawdust before adsorption studies.

Inducement of zinc (Zn^{2+}) into an aqueous solution

2.085g of Zinc chloride ($ZnCl_2$) salt was dissolved in 1L of deionized water to obtain a 1000ppm stock solution of Zn^{2+}. Standard dilution formula (equation 1) was applied to prepare 50ppm used as the working solution by pipetting 50ml of the 1000ppm metal stock solution into a beaker (1L) and was made up to the final volume using distilled water. 50ml from the new working solution was transferred into a 100ml Pyrex glass conical flask, and this was used for the batch biosorption studies. All chemicals used were of analytical grade.

$$C_1V_1 = C_2V_2 \quad (1)$$

Where C_1 is the stock concentration (1000ppm), V_1 is the new stock volume required, C_2 is the concentration of the working solution needed (50ppm), V_2 is the final volume of dilution (1000ml)

Batch biosorption studies

In this study, batch experiments were performed by adding 0.2g of the biosorbent (treated and untreated sawdust) into the pyres glass conical flask containing 50ml of the metal solution and placed on an orbital shaker operating at 120 rpm (rotation per minute) at room temperature. The effect of pH on the adsorption capacity of the biosorbent was determined by adding 0.2g of the sawdust (treated and untreated) into six conical flasks containing the metal solution (50ppm) at different pH values. The working solutions' pH was adjusted (to values of 2, 3, 4) using 0.1M NaOH and 0.1M HCL, monitored with a pocket-sized Hanna pH meter. The six biosorption mixtures were agitated for 300mins and analyzed at different pH. For contact time, the metal solution's pH in the six conical flasks was adjusted to 4, and 0.2g of the sawdust was added to each solution. The samples were agitated and analyzed at different contact times (60, 90 and 120 minutes). For both studies, samples were filtered using Whatman filter paper, and the supernatant was analyzed for Zn^{2+} by an atomic absorption spectrometer (Thermo Scientific S4 AA System). The biosorption capacity (mg/g) and removal efficiency (% R) was calculated using the following equation.

$$qe = \frac{(Ci-Ce)V}{m} \tag{2}$$

$$\text{Removal efficiency} = \frac{Ci-Ce}{Ci}\ x\ 100 \tag{3}$$

Where qe is the amount of metal ion adsorbed on the biosorbent (mg/g), C_i and C_e are the initial and final ion concentrations (mg/L) respectively, V is the volume of the medium used (L), and m is the amount of biomass used (g).

Data analysis

This study's experimental design was a 2 x 2 x 3 factorial experiment; two sawdust species, two treatments (treated and untreated for the wood species), and three levels of pH and time as factors. Descriptive statistics to present the mean and standard deviation for each wood species were performed using the "rstatix package"[20]. Analysis of variance was tested using the "RcmdrMisc package"[21] in the R system for statistical computing (R Core Team, 2020).

Results and discussion

Effect of contact time

Figure 1 presents the mean values for the removal efficiency of treated and untreated sawdust of *Gmelina arborea and Albizia zygia* at different contact times. The sawdust of *Albizia zygia* had a slightly higher removal efficiency (64.82%) than the sawdust of *Gmelina arborea* (64.24%). Time had no significant influence on the adsorption capacity of the species. The treated sawdust of *Albizia zygia* had an average removal efficiency of 62.50%, with its highest (63.33%) % removal recorded at 90 minutes contact time. However, the untreated *Albizia zygia* sawdust had an average removal efficiency of 67.14%, with the highest (67.29%) % removal observed at 120 minutes contact time. For *Gmelina arborea*, the result revealed that the treated sawdust samples had an average removal efficiency of 61.18 %, with its highest (61.46 %) removal efficiency observed at 120 minutes contact time. On the other hand, the untreated sawdust samples had an average removal efficiency of 67.29 mg/g, with its highest (68.25 mg/g) recorded at 90 minutes. Contact time is an "important parameter that determines the best operational conditions in a continuous process of ions removal"[22]. The time to reach maximum biosorption depends on the type of biosorbent, metal ion, and interaction[15]. Biosorption consists of two phases: an initial rapid stage, where approximately 90% of the metal-binding occurs due to free active sites available for metal ion biosorption[15], and in the slow phase, biosorption decreases due to saturation of the metal-binding sites[23]. In this study, it was observed that the highest removal efficiency (68.25 mg/g) was recorded at 90 minutes, which can be presumed to be the equilibrium time where equilibrium metal ion concentration was achieved. This equilibrium time agrees with Shobana[24], who recorded the highest adsorption (70.10 mg/g) at 90 minutes. However, the equilibrium time observed in this study is higher than 30 minutes reported by[23], who used microorganisms (*Pseudomonas aeruginosa and Bacillus cereus*) to remove Zn (II) from aqueous solutions.

The result of ANOVA presented in Table 1 showed that only the effect of treatment was significantly different ($P < 0.05$). The treatment's main effect yielded $F (1, 24) = 14.735$, $p < 0.05$, indicating that the average removal efficiency of untreated sawdust samples was significantly higher than that of the treated samples.

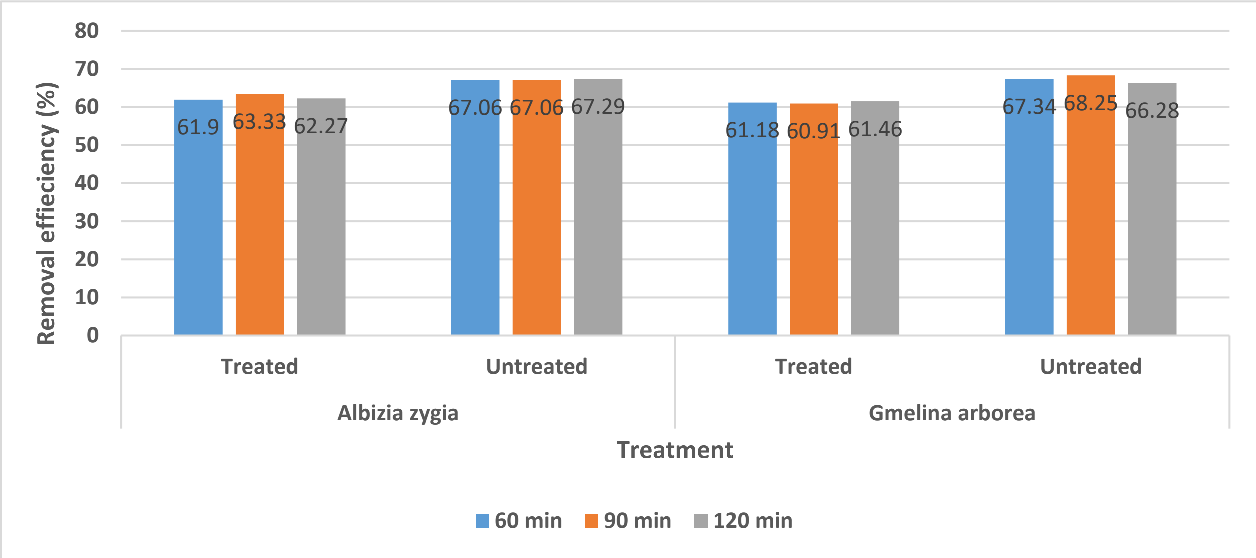

Figure 1. Removal efficiency of treated and untreated sawdust at different contact time.

Table 1. Analysis of variance showing the effect of species, treatment and contact time.

Source of Variation	Df	Absorption rate
Species	1	0.173ns
Treatment	1	14.735**
Contact time	2	0.066ns
Species * Treatment	1	0.274ns
Species * Contact time	2	0.021ns
Treatment * Contact time	2	0.027ns
Species * Treatment * Contact time	2	0.161ns
Error	24	
Total	36	

** Significant at $p < 0.05$
ns – not significant

Effect of pH

Results from the study showed that pH had significant effects on the adsorbent potential of the sawdust. The mean values for the removal efficiency of treated and untreated sawdust of *Gmelina arborea and Albizia zygia* at different pH levels are presented in Figure 2. For *Albizia zygia*, it was observed that the treated sawdust had an average removal efficiency of 67.10 %, with its highest (67.42 %) removal efficiency recorded at pH 4. On the other hand, the untreated *Albizia zygia* sawdust had an average removal efficiency of 70.64 %, in which the highest (71.60 %) removal efficiency was observed at pH 4. For *Gmelina arborea*, the result showed that the treated sawdust samples had an average removal efficiency of 67.66 %, with its highest (68.36 %) removal efficiency observed at pH 4. On the other hand, the untreated sawdust samples had an average removal efficiency of 75.71 %, with its highest (76.26 %) removal efficiency recorded at pH 4.

pH indicates the degree of acidity or alkalinity of a solution on a logarithmic scale where seven is neutral, lower values are acidic, and higher values are alkaline. pH is one of the essential physicochemical factors influencing the biosorption process because of its role in metal chemical speciation and solubility and the total charge of the biosorbent[15,25]. At low pH (acidic condition), the hydronium ions (H_3O^+) are attracted to the biosorbent. Therefore, there will be a competition between the protons in the solution and the positively charged metal ions at the binding sites, which will reduce the biosorption process[15,26]. However, there will be an increased amount of hydroxyl ions (OH-) attracting positive-charged metal at higher pH, thus increasing biosorption[25]. Studies have reported that at higher pH in the Alkaline range, metal ions precipitate, and as a result, halts the biosorption process[25,27]. Therefore, this study considered three pH levels (i.e., pH 2, 3, and 4) with pH 4 as optimum[27]. This study agrees with the above explanation that because the rate of adsorption increased as pH increased, with pH 4 having the highest adsorption rate for both treated and untreated sawdust. This study also aligns with previous findings[24,28,29].

The result of ANOVA as presented in Table 2 showed that there was a statistically significant interaction between species and treatment during adsorption F (1, 24) = 50.676, $p < 0.05$, indicating that the average removal efficiency of treated and untreated sawdust samples was significantly different in both wood species.

Table 2. Analysis of variance showing the effect of species, treatment, and pH levels.

Source of Variation	Df	Absorption rate
Species	1	78.792**
Treatment	1	335.414**
pH level	2	4.087*
Species * Treatment	1	50.676**
Species * pH level	2	2.110ns
Treatment * pH level	2	0.165ns
Species * Treatment * pH level	2	0.585ns
Error	24	
Total	36	

*significant at $p < 0.01$, **significant at $p < 0.05$, ns – not significant

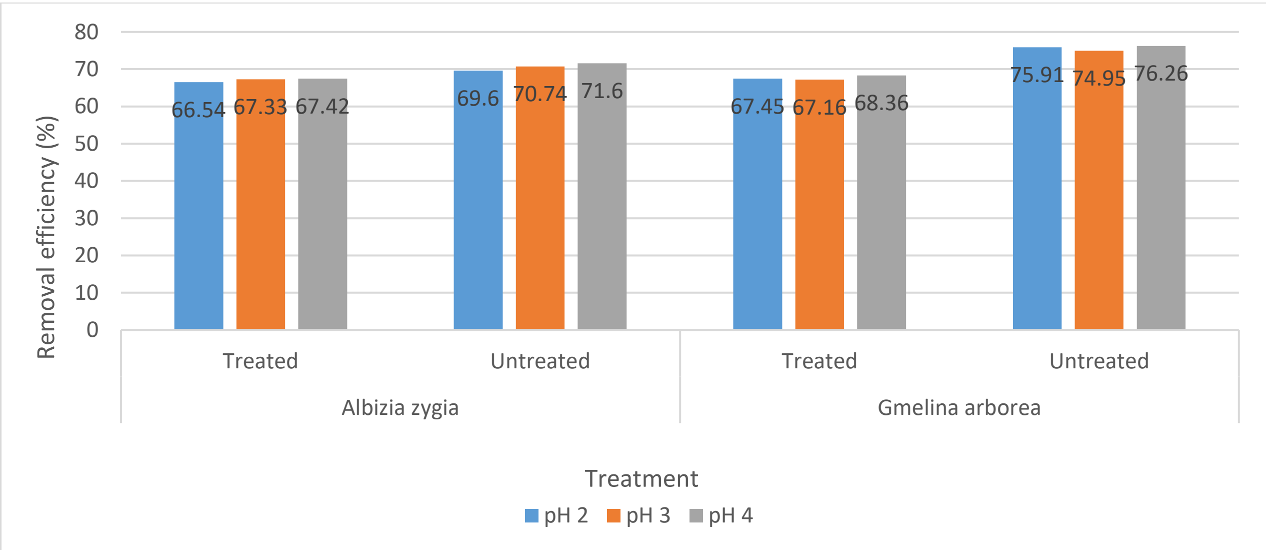

Figure 2. The removal efficiency of treated and untreated sawdust at different pH levels.

The sawdust of both wood species used in this study showed great potential as a low-cost adsorbent for industrial application. It compares favourably with different materials used in removing Zn (II), as presented in Table 3.

Table 3. Biosorption of zinc ions using various biosorbents from the literature.

Adsorbent	Type	Adsorption capacity (mg/g)	pH	Initial concentration range (mg l^{-1})	Reference
Bagasse carbon	Activated carbon	31.11	4.5	1 – 1000	27

Fontinalis antipyretica	Aquatic moss	15.0	5.0	100	[30]
Botrytis cinerea	Biomass	12.98	5.0 - 6.0	100	[31]
Sea nodule residue	Solid waste	21.09	na.	na.	[32]
Acinetobacter sp	Bacteria	36.0	na.	na.	[33]
Pinus sylvestris bark	Wood waste	40.0	6.1	1045	[34]
Albizia zygia sawdust	Wood waste	17.22	2.0 - 4.0	50	Current study
Gmelina arborea sawdust	Wood waste	17.92	2.0 - 4.0	50	Current study

na. = not available

Conclusions

Sawdust is a cheap and effective adsorbent for the removal of Zn (II) from contaminated water. Therefore, sawdust that is customarily burnt and contributes to air pollution can be harnessed to improve water quality at a comparatively lower cost. This study showed that the untreated sawdust had higher adsorption properties. Future studies will be interesting to compare with other pre-treatment methods and consider other factors affecting adsorption, such as the effect of temperature, initial metal concentration, biosorbent dose, agitation speed. Another critical direction can be applying this biosorbent in real wastewaters/effluents as literature reveal that real wastewaters/effluents affect biosorption due to other metals' presence. However, based on availability, cost-effectiveness, ability to be recovered and reused, sawdust of *Albizia zygia* and *Gmelina arborea* can be recommended as effective adsorbents in the treatment of water towards ensuring that quality water is available for humans, plants, and animals.

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