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The Utilization of Brewery Spent Grains for the Removal of Cd^{2+}; Ni^{2+} and Pb^{2+} from Brewery Effluents: A Case Study of Nigerian Brewery, Kaduna

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Abstract
This study explores the potential use of brewery-spent grains as an effective sorbent for the removal of Cd^{2+}, Ni^{2+}, and Pb^{2+} from brewery effluents using batch adsorption experiment. The research utilizes Nigerian Brewery, Kaduna, as a case study in order to assess the efficiency of this method. Results obtained revealed that the highest removal efficiency were 99.9 %, 96.5 % and 86.7 % for Pb^{2+}, Ni^{2+} and Cd^{2+} with adsorption capacity of 99.9 mgg^{-1}, 19.3 mgg^{-1} and 17.4 mgg^{-1} respectively. The removal of the contaminants by the adsorbents was dependent on varying conditions of temperature, pH, contact times, initial concentration and adsorbent dose. Furthermore, Sodium hydroxide treated spent grain demonstrated the best sorbent ability, having the highest efficiency removal of 99.0 %, 98.2 % and 96.5 % with the adsorption capacity of 9.90 mgg^{-1}, 9.82 mgg^{-1} and 9.65 mgg^{-1} respectively. Results indicate that brewery-spent grains have a high affinity for the aforementioned heavy metals and can effectively remove them from the effluents. This suggests that brewery-spent grains have the potential to be a cost-effective and environmentally friendly solution for the treatment of brewery effluents. Further research and optimization of this method could lead to its implementation as a sustainable and efficient way to remove heavy metals from industrial wastewater.

Keywords: Kaduna Brewery, Adsorption, Nickel, Cadmium, Lead

Introduction

Pollutants released into the aquatic environment can be attributed to growing human population, industrialisation, technological development, exploration, agricultural and domestic waste run-off [1]. Heavy metals are one of the constituents of these pollutants and they posed a threat to human life because of their toxicity, non-degradability, persistency and inclination to bio-magnification and bioaccumulation [2]. Acute concentration of heavy metals could lead to the damage of central nervous functions, cardio-vascular and gastro-intestinal systems, lungs, kidneys, liver, endocrine glands and bones [3]. Brewery industries produce a substantial effluent which could contain heavy metals and organic matter originating from the brewing process that lead to depletion of oxygen content of water bodies when discharged into them [4]. It is a usual practice that Rivers, lakes and other water bodies serve as source of effluent disposal by most industries in the world and Nigeria is not an exception [5]. Today, water has become a threatened resource in many parts of the world; hence the development and application of smart ground-breaking strategies to treat wastewater for re-use is a priority [6]. The brewery industry is one of the largest industrial users of water, but its effluent is characterised by high levels of organic matter and heavy metal contaminants which require remediation [7]. Brewers spent grain is an efficient absorber for toxic heavy metal ions, the adsorption properties of two different brewers spent grains show their efficiency as absorbers for simulated and real surface water. The result obtained demonstrated different adsorption behaviour despite almost identical chemistry [8]. Brewery spent grains (BSG) is the major by-product of the brewing industry, representing around 85% of the total by-products generated [9]. The aim of this research is to explore the potential of brewery spent grain (BSG) as one of the adsorbents for the removal of lead, cadmium and nickel from brewery wastewater.

Materials and Methods

Sample collection and preparation

The raw wastewater sample was collected by lowering a pre-cleaned 4L plastic gallon at the discharge point at the Nigerian Breweries at Kakuri in Kaduna Metropolis by allowing it to over flow before withdrawing, then the plastic gallon was sealed and stored at 4°C in the refrigerator for further analysis [10]. The brewery spent grains was similarly obtained from the Nigerian Breweries at Kudenda, Kaduna. 14g of the brewery spent grains were mixed with a 1M NaOH solution for 4-5 hours at room temperature to enhance its metal sorption capacity. The excess of alkaline solution was removed by washing spent grains with distilled water until it was completely free from the base in successive washings. This material was designated as NaOH treated spent grain (NaOH TSG). TSG was then dried in an oven at 90°C for 5 hours. The dried spent grains was pulverized and sieved with a 40 micron mesh size [11]. The same procedure were used for the preparation of sodium chloride treated spent grains (NaCl TSG), sulphuric acid + sodium hydroxide treated spent grain (H_2SO_4 + NaOH TSG), sodium chloride + Citric acid treated spent grain (NaCl + $C_6H_8O_7$ TSG), sodium carbonate treated spent grains (Na_2CO_3 TSG) and ammonium chloride treated spent grains (NH_4Cl TSG).

Determination of heavy metals in brewery wastewater

A quantity of 200 mL of well mixed sample solution of the brewery effluent was measured into a cleaned 250 mL beaker, and then 2 mL of concentrated nitric acid was introduced into the sample solution and was heated on a hot plate to evaporation in a fume cupboard to less than 20 mL. The digested sample was further reconstituted with 20 mL distilled water and quantitatively transferred to a 50 mL volumetric flask and made to the mark with distilled water, and was kept in a pre-cleaned 60 mL syrup bottle for analysis using Atomic Absorption Spectrophotometer [12].

Characterization of Adsorbent

The brewery spent grains adsorbents before adsorption were characterized using Agilent Technology Cary 630 model of Fourier Transform Infrared Spectroscopy (FT-IR) in order to identify the functional groups of the adsorbents that might be involved in the binding of metal ions [13].

Batch adsorption Experiment

Sorption studies were conducted by the batch technique as reported by Itodo *et al.* [14] using serial dilution of metal ions solution to determine the adsorption rate of the metal ions onto the adsorbents in 250 mL glass flask. The flasks containing the metal ions solutions and weighed mass of the adsorbent were shaken at a constant rate at 200 rpm, allowing sufficient time for adsorption equilibrium. All adsorption experiments were carried out using an orbital shaker. The pH of the solution was measured by digital electronic pH meter (Trulab), and adjusted by the addition of 1M sodium hydroxide solution or dilute hydrochloric acid solution in drops. The flasks were plugged and kept closed to avoid the fluctuation of pH due to the exchange of gases during the experiment. The effects of various parameters on the rate of adsorption process were observed by varying contact time (30, 60, 90, 120, and 150 minutes), adsorbent concentration (0.5, 1.0, 1.5, 2.0, 2.5 g), temperature (308, 318, 328 and 338 K), initial metal ion concentration (5, 10, 15, 20, 25, 50,100,150, 200 and 250 mg/L and pH (2.0–10.0) of the solution. The solution volume (V) was kept constant [11]. The solutions were filtered using Whatman 42 filter paper after the adsorption experiments and the filtrates were digested in 250 mL beakers by the addition of 5- 10 mL of concentrated nitric acid. The solutions were then heated on a hot plate in a fume cupboard and allowed to evaporate to a volume of less than 50 mL and were thereafter made up with distilled water to 50 mL mark, before being transferred to pre-cleaned syrup sample bottles for Atomic Absorption Spectroscopic (AAS) to determine the concentration of the metal ions remaining in the solution. The amount of metal ion adsorbed per unit mass was calculated as

$$Qe = \frac{(Ci - Ce)V}{m} \quad (1)$$

Where Ci and Ce are the initial and equilibrium concentration (mgL^{-1}), m is the mass of the adsorbent (g) and V is the volume of the solution (mL). The Percentage metal ion removal (%MR) was calculated using the equation

$$\%\ MR = \frac{Ci - Ce}{Ci} X100 \quad (2)$$

Results and Discussion

Concentration of heavy metals in the effluents

Table 1 shows the concentration of the heavy metals studied (lead, nickel and cadmium) in the brewery wastewater. The results shows that nickel has the highest concentration of 1.46 mgL^{-1} in the effluent discharge which is above the minimum standard set by WHO and USEPA, also, the concentrations of lead at 0.756 mgL^{-1} and cadmium at 0.343 mgL^{-1} were above the limits set by aforementioned international bodies.

Table 1: Concentration of heavy metals in the effluent of Nigerian Breweries at Kakuri, Kaduna

Element	Concentration (mgL^{-1})	WHO	USEPA (2009)	FEPA, (1999)
Nickel	1.461	0.007mg/L	≤ 0.1mg/L	<1mg/L
Lead	0.756	0.01mg/L	≤ 0.05mg/L	<1mg/L
Cadmium	0.343	0.003mg/L	≤ 0.01mg/L	<1mg/L

Spectroscopic Characterization of the Adsorbent

Figures 1-7 show the FT-IR results for the brewery spent grains before adsorption with some important peaks which include; the broad peaks at 3200-3400 cm^{-1} are attributed to the hydroxyl groups which formed hydrogen bonds between carbohydrate molecules in spent grains; they are rich in hydroxyl group (3283.8 cm^{-1}) in brewery spent grain which may have been caused by the stretching vibration of the C-OH bond in cellulose and hemicellulose of brewery spent grains. The absorption peaks at 2922.2 cm^{-1} and 2855.1 cm^{-1} are caused by asymmetric-CH_2 stretching vibration of alkanes and =C-H stretching vibration of alkenes respectively; the absorption peaks at 1744.4 cm^{-1} are attributed to carbonyl C=O group in carboxyl, aldehyde or ketones; the absorption peaks at 1028.7 are mainly caused by C-O bonds. Therefore, brewery spent grain

contains hydroxyl, carboxyl and other active functional groups, which can participate in active adsorption [15].
All functional groups aforementioned, their types of vibrations, wave number and intensity found in brewery spent grains are as presented in Table 2. Figure 2 illustrated that the peak at 3283.8 cm^{-1} indicates the presence of O-H stretching vibration in hydroxyl group for alcohols mainly due to the presence of cellulose molecules whereas the peak at 2922.2 cm^{-1} identifies the presence of C-H stretching vibration for alkanes due to elongation and bending vibration of the -CH_3 methyl group [16] while the peak at 2855.1 cm^{-1} indicates the presence of =C-H stretching vibration for alkene. The peak at 1744.4 cm^{-1} suggests the presence of ∂- bonding in –C=O carbonyl group, while the peak at 1625.1 cm^{-1} indicates the C-O stretching vibration. The FTIR results presented here agreed with similar works done by [17]. From Figure 2, the peak at 3306.1cm^{-1} indicates the presence of O-H stretching vibration in hydroxyl group for alcohol and carboxylic acids. The peak at 2922.2 cm^{-1} identifies the presence of C-H Stretching vibration for alkanes, while the peak at 2855.1 cm^{-1} indicates the presence of =C-H stretching vibration for alkenes. The peak at 1744.4 cm^{-1} suggests the presence –C=O stretching vibration for carbonyl groups which may be attributed to hemicellulose and lignin aromatic group and this is in agreement with the works of [18], while the peak at 1625.1 cm^{-1} indicates the C-O stretching vibration.

Table 2: Functional groups found in Fourier Transform Infrared Analysis of the untreated Brewery Spent Grains before the adsorption experiment

Signal	Wavenumber cm^{-1}	Functional groups
1	3283.8	O-H stretching
2	2922.2	C-H asymmetric stretching
3	2855.1	=C-H symmetric stretching
4	1625.1	C=O, C=N, C=C stretching
5	1520.8	N-H bending, C=C, C-N stretching
6	1446.2	C-H bending
7	1237.5	O-H, bending, C-N, C-O stretching
8	1155.5	C-N, C-O stretching
9	1028.7	C-N, C-O stretching

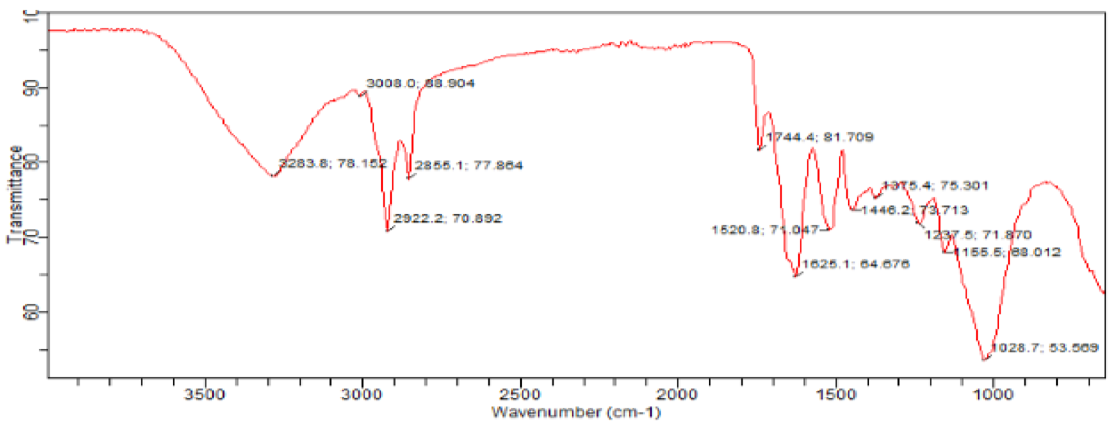

Figure 1: FTIR spectra of untreated Brewery Spent Grains before adsorption

According to Rudi *et al.* [19], the treatment of brewery spent grains by sodium hydroxide, weakened the stretching vibration of the benzene ring skeleton, thus releasing more hemicellulose and cellulose, that are rich in hydroxyl group, which is an indication that the lignin in brewery spent grains could be degraded by sodium hydroxide. Therefore, sodium hydroxide treatment of brewery spent grain degraded the lignin, consequently made the treated spent grains to have more porous structure, which enhanced the adsorption of the heavy metals as evident in this study. Hence, this could be attributable to the excellent sorbent ability of sodium hydroxide treated spent grains as the best adsorbent among the seven brewery spent grains based adsorbents prepared and used in this study.

From Figure 3, the peak at 3280.1cm^{-1} indicates the presence of O-H stretching vibration in hydroxyl group for alcohols, whereas the peak at 2922.2 cm^{-1} identifies the presence of C-H Stretching vibration for alkanes, while the peak at 2855.1 cm^{-1} indicates the presence of =C-H stretching vibration for alkenes. The peak at 1744.4 cm^{-1} suggests the presence of ∂- bonding in –C=O of carbonyl group, while the peak at 1625.1 cm^{-1}

indicates the C-O stretching vibration. From Figure 4, the peak at 3280.1cm-1 indicates the presence of O-H stretching vibration in hydroxyl group for alcohols, whereas the peak at 2922.7cm-1 identifies the presence of C-H Stretching vibration for alkanes, while the peak at 2855.1cm-1 indicates the presence of =C-H stretching vibration for alkenes. The peak at 1740.7 suggests the presence of –C=O bonding in carbonyl group, while the peak at 1625.1 cm-1 indicates the C-O stretching vibration. From Figure 5, the peak at 3280.1cm-1 indicates the presence of O-H stretching vibration in hydroxyl group for alcohols, whereas the peak at 2922.2cm-1 identifies the presence of C-H Stretching vibration for alkanes, while the peak at 2855.1cm-1 indicates the presence of =C-H stretching vibration for alkenes. The peak at 1740.7 cm-1 suggests the presence of ∂- bonding in –C=O of carbonyl compounds, while the peak at 1625.1 cm-1 indicates the C-O stretching vibration.

Table 3: Functional groups found in Fourier Transform Infrared analysis of the NaOH Treated Spent Grains before the adsorption experiment

Signal	Wavenumber cm-1	Functional groups
1	3306.1cm-1	O-H stretching
2	2922.2	C-H asymmetric stretching
3	2855.1	=C-H symmetric stretching
4	1744.4	C=O, C=N, C=C stretching
5	1625.1	N-H bending, C=C, C-N stretching
6	1457.4	C-H bending
7	1237.5	O-H, bending, C-N, C-O stretching
8	1159.5	C-N, C-O stretching
9	1025.7	C-N, C-O stretching

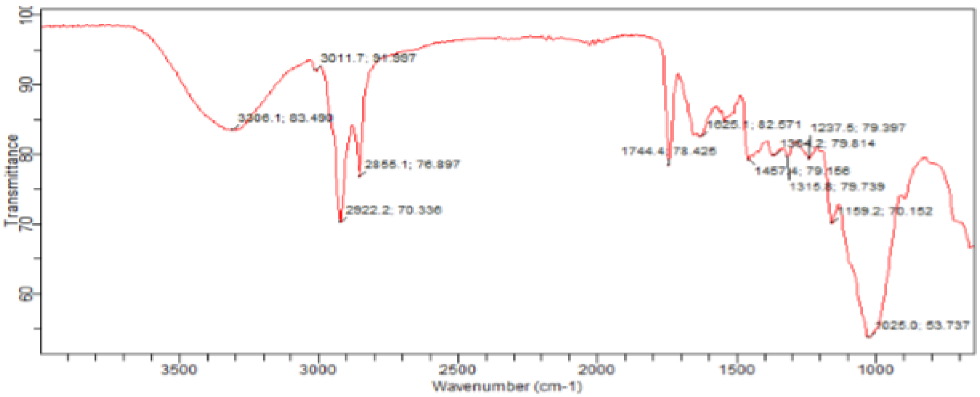

Figure 2: Fourier Transform Infrared Spectrum of NaOH Treated Spent Grains before Adsorption

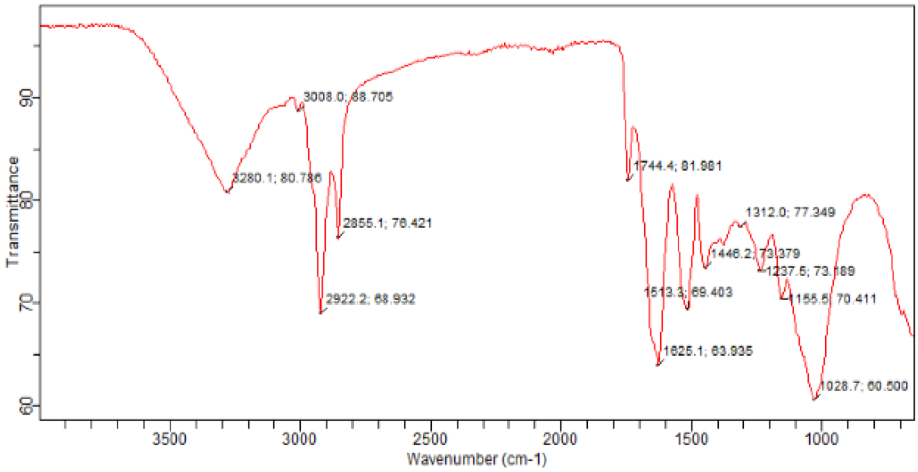

Figure 3: Fourier Transform Infrared Spectrum of Na_2CO_3 Treated Spent Grains before Adsorption

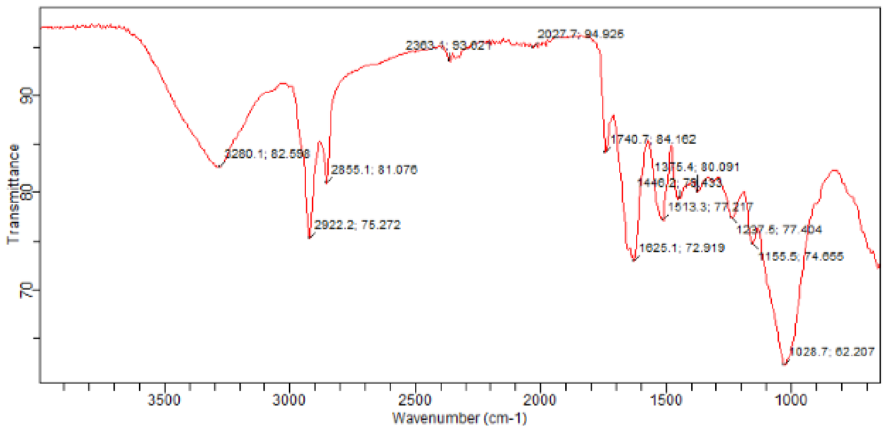

Figure 4: Fourier Transform Infrared Spectrum of NaCl Treated Spent Grains before Adsorption

From Figure 6, the peak at 3283.8 cm^{-1} indicates the presence of O-H stretching vibration in hydroxyl group for carboxylic acids, whereas the peak at 2922.2 cm^{-1} identifies the presence of C-H Stretching vibration for alkanes, while the peak at 2855.1cm^{-1} indicates the presence of =C-H stretching vibration for alkenes. The peak at 1740.7 cm^{-1} suggests the presence of –C=O stretching vibration of carbonyl group, while the peak at 1625.1 cm^{-1} indicates the C-O stretching vibration. The treatment of brewery spent grains by dilute sulphuric acid could lead to a significant decrement in the content of hydroxyl and methyl group, indicating that hemicellulose in brewery spent grain could be hydrolyze
.

From Figure 7, the peak at 3280.1 cm^{-1} indicates the presence of O-H stretching vibration in hydroxyl group for alcohols, whereas the peak at 2922.2 cm^{-1} identifies the presence of C-H stretching vibration for alkanes, while the peak at 2855.1cm^{-1} indicates the presence of =C-H stretching vibration for alkenes. The peak at 1744.4 cm^{-1} suggests the presence of ∂- bonding in –C=O group of carbonyl compounds , while the peak at 1625.1 cm^{-1} indicates the C-O stretching vibration.

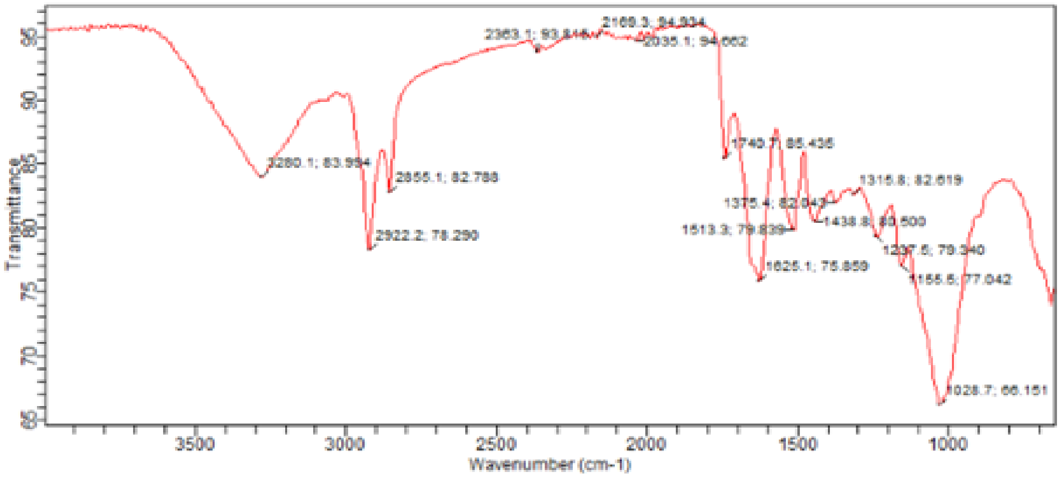

Figure 5: Fourier Transform Infrared Spectrum of NH_4ClTreated Spent Grains before Adsorption

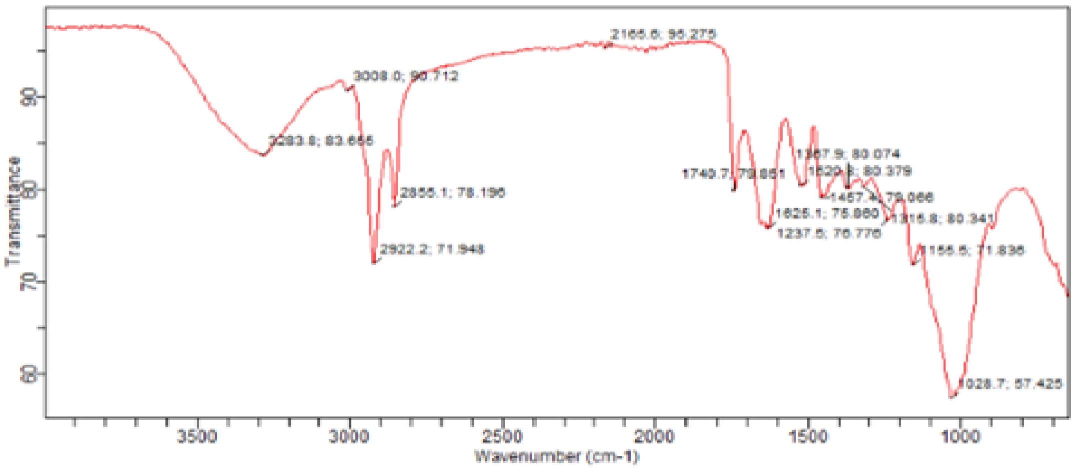

Figure 6: Fourier Transform Infrared Spectrum of H_2SO_4 + NaOH Treated Spent Grains before Adsorption

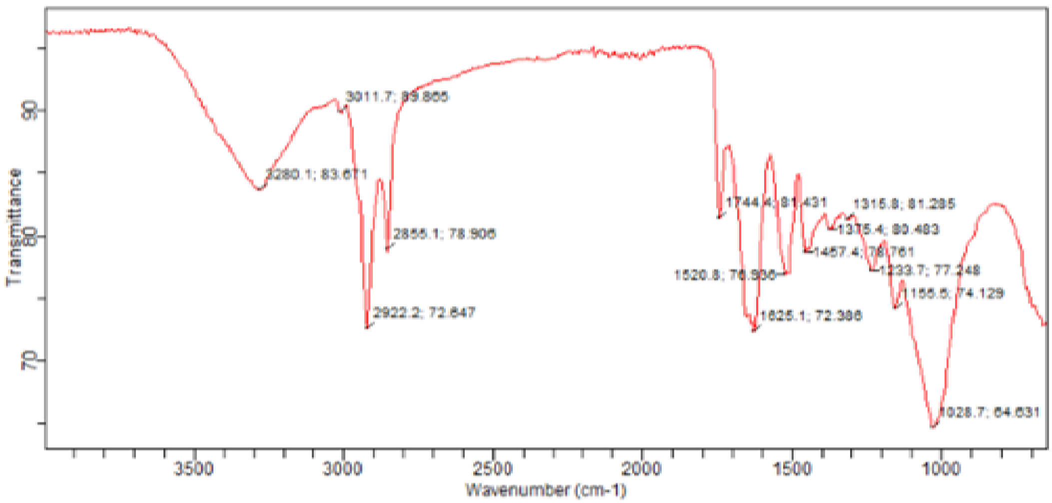

Figure 7: Fourier Transform Infrared Spectrum of Citric + NaCl Treated Spent Grains before Adsorption

Pb^{2+}Adsorption Optimization

Adsorption optimization experiment was conducted for the adsorption of pb^{2+} onto brewery spent grain by varying conditions of different parameters, pH, time, adsorbent dose, temperature and initial metal ion concentration understudied. The Table 4 revealed that an increase in the mass of adsorbent dose, which in this case is the unmodified brewery spent grains, has resulted to a corresponding increase in pb^{2+} removal efficiency from 89.1 % mass removal of metal ion in the solution at 0.5 g of the adsorbent dose to 99.3 % removal at 2.5 g of the adsorbent dose.

Table 4: Effect of adsorbent dosage on the adsorption of Pb^{2+} onto unmodified brewery spent grain

Mass of adsorbent(g)	Temp(°C)	pH	Time (min)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	$\%MR$= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	27	7.5	102	100	10.9	89.1	89.1	0.2	35.6
1.0	27	7.5	102	100	5.14	94.9	94.9	0.2	19.0
1.5	27	7.5	102	100	3.00	97.0	97.0	0.2	12.9
2.0	27	7.5	102	100	2.08	97.9	97.9	0.2	9.79
2.5	27	7.5	102	100	0.714	99.3	99.3	0.2	7.94

From Table 5, the metal ion removal efficiency in the solution rise from 2% at the initial metal ion concentration of 5mgL^{-1} to 99.9 % at the initial metal ion concentration of250 mgL^{-1}. It can be seen that adsorption capacity of the brewery spent grains increases as the initial concentration of pb^{2+} increased, the adsorption capacity increased from 0.737 mgg^{-1} to 99.9 mgg^{-1}. Increase in metal ions concentration results in increase in number of available molecules per binding sites of the adsorbent. Increase in initial metal ions concentration enhances the interaction between the metal molecules and the surface of the adsorbent meaning; it provides a driving force to overcome mass transfer resistance between the adsorbent and its medium [19]. The data presented in Table 6 showed that adsorption of metal ion by the brewery spent grains increased, with increase in temperature from room temperature to 35°C, and this pattern is common to the bio sorption of most metal ions from their solution [20]. However, the magnitude of such increase continues to decline as temperatures were increased from 45°C to 55°C. This is because with increasing temperature, the attractive forces between biomass surface and metal ions are weakened and the sorption decreases [21].

Table 5: Effect of initial metal ion concentration on the adsorption of Pb^{2+} onto unmodified brewery spent grains

Ci(mg/L)	Temp(°C)	pH	Time (min)	Mass of adsorbent(g)	Ce(mg/L)	Ci-Ce	%MR= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)V/m
5	27	7.5	102	0.5	4.90	0.1	2	0.2	0.04
10	27	7.5	102	0.5	8.16	1.84	18.4	0.2	0.737
15	27	7.5	102	0.5	7.52	7.48	49.8	0.2	2.99
20	27	7.5	102	0.5	8.12	11.9	59.4	0.2	4.75
25	27	7.5	102	0.5	7.99	17.0	68.1	0.2	6.81
50	27	7.5	102	0.5	0.134	49.9	99.7	0.2	19.9
100	27	7.5	102	0.5	1.05	99.0	99.0	0.2	39.6
150	27	7.5	102	0.5	0.731	149	99.5	0.2	59.7
200	27	7.5	102	0.5	0.940	199	99.5	0.2	79.6
250	27	7.5	102	0.5	0.304	249	99.9	0.2	99.9

As temperature increased above 60°C, after an initial slow sorption was observed, it was followed by a rapid sorption process to reach equilibrium. The equilibrium concentrations for higher temperatures (60°C and above) were not significantly different for those of lower temperatures, indicating that temperature increases were observed to be in two phases for lower temperatures and for higher temperatures. The result here is comparable to the work of Wang *et al.* [22] who deduced that modification of temperature was a key parameter affecting the adsorption performance of alkaline spent grain with the increase, this is due to the activation of partially inactivated adsorption sites with the increase of temperature, which generates more adsorption sites and increases its adsorption effect on methylene blue. As the temperature continues to rise, the adsorption sites tend to be saturated, and the number remains static.

From the Table 7, the lead (II) ions removal efficiency onto brewery spent grain at pH 4 is 98.9 % which is higher and an improvement, compared to previous work done on lead adsorption onto spent grain by [8], where he recorded 96.5 % removal efficiency at the same pH level. However, as pH value increases from 4 to 6, a marginal diminishing of removal efficiency was observed. This slight decrement interestingly varnished as the pH value increases from 8-10, with maximum removal efficiency of 99.5 % at the pH 10. At pH 2, the least metal ion removal efficiency was observed, probably, this can be explained due to competition between protons and metal ions for capturing same sites of the adsorbent, thus resulting to low adsorption of the metal. The results obtained here are congruent with the principle of bio-sorption with pH variation. The effect of pH on adsorption of metal ions onto activated teff straw was studied by [23], results revealed that the removal of metal ions was strongly dependent on the pH of the solution.

Table 6: Effect of temperature on the adsorption of Pb^{2+} onto unmodified brewery spent grain

Mass of adsorbent(g)	Temp(°C)	pH	Time (min)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	%MR= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	35	7.5	102	100	4.36	95.6	95.6	0.2	38.3
0.5	45	7.5	102	100	12.9	87.1	87.1	0.2	34.8
0.5	55	7.5	102	100	11.0	89.0	89.0	0.2	35.6
0.5	65	7.5	102	100	2.63	97.4	97.4	0.2	38.9

Table 7: Effect of pH on the adsorption of Pb^{2+} onto unmodified brewery spent grains

Mass of adsorbent(g)	Temp(°C)	pH	Time (min)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	%MR= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	27	2.0	102	100	28.4	71.6	71.6	0.2	28.6
0.5	27	4.0	102	100	1.06	98.9	98.9	0.2	39.6
0.5	27	6.0	102	100	5.58	94.4	94.4	0.2	37.8
0.5	27	8.0	102	100	0.687	99.3	99.3	0.2	39.7
0.5	27	10	102	100	0.492	99.5	99.5	0.2	39.8

Wassie and Srivastava, [24] conducted the experiment at different pH 1.0–11.0, and the maximum removal capacity of activated teff straw was found to be at pH 6.5.The pH of the metal ion solution is an important parameter for adsorption of metal ions because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate [25]. The adsorption of metal ions increased with an increase in the pH of the solution in the basic medium [26]. In the course of this study, results revealed that the removal of metal ions was strongly dependent on the pH of the solution. From the Table 8, the maximum removal efficiency of 99.7 % was recorded within the first sixty minutes. And adsorption is usually higher initially when adsorption process begins because numerous active sites are available on the adsorbent. With time, the active sites get exhausted and the rate at which the adsorbate is moved from the external to the internal sites of the adsorbent controls the sorption process. The fast adsorption at the initial stages is due to the presence of vacant and abundant active sites on the adsorbents which becomes used up with time and becomes saturated thereby attaining equilibrium [27]. From Table 8, the Nickel (II) ions removal efficiency onto brewery spent grain recorded a maximum removal of 96.5 % at pH 10. It was observed that the percentage removal of Ni (II) ions on the adsorbent showed an increase with increase in initial pH of solution. With an increase in initial pH of solution from 2.0 to 10.0, the percentage removal of Ni (II) increased from 1.75-96.5 %, while in Figure 4, the adsorption capacity increased from 0.358 to19.3 mgg^{-1}.

Table 8: Effect of time on the adsorption of Pb^{2+} onto unmodified brewery spent grains

Mass of adsorbent(g)	Temp(°C)	pH	Time (mins)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	%Mr= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	27	7.5	30	100	0.464	99.5	99.5	0.2	39.8
0.5	27	7.5	60	100	0.292	99.7	99.7	0.2	39.9
0.5	27	7.5	90	100	1.78	98.2	98.2	0.2	39.3
0.5	27	7.5	120	100	0.544	99.5	99.5	0.2	39.8
0.5	27	7.5	150	100	2.42	97.6	97.6	0.2	39.0

Table 9: Effect of pH on the adsorption of Ni^{2+} onto unmodified brewery spent grains

Mass of adsorbent(g)	Temp(°C)	pH	Time (mins)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	%MR= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	27	2.0	102	50	49.1	0.895	1.75	0.2	0.358
0.5	27	4.0	102	50	47.5	2.53	5.05	0.2	1.01
0.5	27	6.0	102	50	40.6	9.43	18.9	0.2	3.77
0.5	27	8.0	102	50	38.2	11.8	23.5	0.2	4.70
0.5	27	10	102	50	1.78	48.2	96.4	0.2	19.3

The low adsorption recorded at lower pH values is simply due to excess H^+ in solution which competes with the metal ions for the active sites of the adsorbent, resulting in a low removal [28]. The results obtained here are congruent with the principle of bio-sorption with pH variation. The effect of pH on adsorption of metal ions onto activated teff straw was studied by Ashagrie [23], results revealed that the removal of metal ions was strongly dependent on the pH of the solution.

This fact was corroborated by Ogbu *et al.* [11], that the initial pH of solution is one of the most important factors in the adsorption of metal ions unto adsorbents as it affects the surface charge of the adsorbent and the degree of ionization and specification of the adsorbate. From Table 10, the solution pH plays a significant role in the sorption process with the maximum removal efficiency of 86.7% of cadmium (II) ions at the pH 10. This is because, the solution pH can affect the surface charge of the adsorbent and the molecular state of the heavy metal [29]. In other words, it interrupts both the solution's chemistry of cadmium nitrate solution used in the experiment and functional groups of the adsorbents. Meanwhile, it seems that the adsorption capacity of the brewery spent grains depends on the pH of the solution. The variation of adsorption capacity of unmodified brewery spent grain for the removal of cadmium (II) is shown in the Table 4.6 with adsorption capacity increasing from 11.8 mgg^{-1} at pH 2 to 17.3 mgg^{-1} at the pH 10. The results as presented above indicate that the basic pH was favorable for the removal of cadmium (II) ions onto unmodified brewery spent grains.

Table 10: Effect of pH on the adsorption of Cd^{2+} onto unmodified brewery spent grains

Mass of adsorbent(g)	Temp(°C)	pH	Time (mins)	Ci(mg/L)	Ce(mg/L)	Ci-Ce	$\%MR$= Ci-Ce/Ci*100	Vol of Solution (L)	Qe=(Ci-Ce)$^{v}/_{m}$
0.5	27	2.0	102	50.0	20.4	29.6	59.2	0.2	11.8
0.5	27	4.0	102	50.0	19.3	30.7	61.3	0.2	12.3
0.5	27	6.0	102	50.0	16.0	34.0	68.0	0.2	13.6
0.5	27	8.0	102	50.0	10.8	39.2	78.4	0.2	15.7
0.5	27	10	102	50.0	6.63	43.4	86.7	0.2	17.3

Batch Adsorption Studies of Heavy Metals on Various Adsorbents

Sorption studies were conducted for the removal of Cd^{2+},Ni^{2+}, and Pb^{2+} at uniform conditions of pH 10,contact time of sixty minutes, initial metal ion concentration of 50 mgL^{-1}, adsorbent dose of 1.0 g, and at a temperature of 27°C using different adsorbents, namely, sodium hydroxide treated spent grains (NaOH TSG), sodium chloride treated spent grains (NaCl TSG), sulphuric acid and sodium hydroxide treated spent grains (H_2SO_4 + NaOH TSG), sodium chloride + Citric acid treated spent grains (NaCl + $C_6H_8O_7$ TSG), sodium carbonate treated spent grains (Na_2CO_3 TSG) and ammonium chloride treated spent grains (NH_4Cl TSG). From Table 11, the results have shown that sodium hydroxide treated spent grains has proven to be a perfect choice as an adsorbent at uniform conditions of pH 10, contact time of sixty minutes, initial metals ions concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0g, and at a temperature of 27°C with metals ion removal efficiency of 94.3 %, 99.0 % and 98.2 % of Cd^{2+}, Ni^{2+}, and Pb^{2+} respectively. The adsorption capacity for each of the element stood at 9.43 mgg^{-1}, 9.90 mgg^{-1} and 9.82mgg^{-1}respectively. From table 12, the results show ammonium chloride treated spent grains as a good adsorbent for the removal of cadmium, nickel and lead at uniform conditions of pH 10, contact time of sixty minutes, initial metals ions concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0 g, and at a temperature of 27°C with metals ion removal efficiency of 80.5 %, 93.8 % and 95.3% of Cd^{2+}, Ni^{2+}, and Pb^{2+} respectively. Each of the aforementioned elements has an adsorption capacity of 8.05 mgg^{-1}, 9.38 mgg^{-1} and 9.53mgg^{-1} respectively. Table 13 has shown that sodium chloride treated spent grains could be used as an effective adsorbent at uniform conditions of pH 10, contact time of sixty minutes, initial metals ions concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0g, and at a temperature of 27°C with metals ion removal efficiency of 93.7 %, 98.2 % and 96.6 % of Cd^{2+}, Ni^{2+}, and Pb^{2} respectively. The adsorption capacity for each of the element stood at 9.37 mgg^{-1}, 9.82 mgg^{-1} and 9.66 mgg^{-1} respectively. From Table 14, the results showed that sodium carbonate treated spent grains as an adsorbent has demonstrated excellent sorbent properties at uniform conditions of pH 10, contact time of sixty minutes, initial metals ions concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0g, and at a temperature of 27°C with metals ion removal efficiency of 96.5 %, 97.2 % and 95.0 % of Cd^{2+}, Ni^{2+}, and Pb^{2+} respectively. The adsorption capacity for each of the element stood at 9.65 mgg^{-1}, 9.72 mgg^{-1} and 95.0 mgg^{-1} respectively.

From Table 15, the results showed that sulphuric acid + sodium hydroxide treated spent grains as an adsorbent of interest at uniform conditions of pH 10, contact time of sixty minutes, initial metals ion concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0g, and at a temperature of 27°C has metals ion removal efficiency of 81.4 %, 90.3 % and 96.9% of Cd^{2+}, Ni^{2+}, and Pb^{2} respectively whereas the adsorption capacity for each of the element stood at 8.14 mgg^{-1}, 9.03 mgg^{-1} and 9.69 mgg^{-1} respectively. From Table 16, the results have shown that Citric acid + NaCl treated spent grains has proven as an excellent adsorbent at uniform conditions of pH 10 contact time of sixty minutes, initial metal ions concentration of 50.0 mgL^{-1}, adsorbent dose of 1.0 g, and at a temperature of 27°C with metals ion removal efficiency of 80.6 %, 93.1 % and 96.4 % of Cd^{2+}, Ni^{2+}, and Pb^{2+} and the adsorption capacity for each of the element stood at 8.06 mgg^{-1}, 9.31 mgg^{-1} and 9.64 mgg^{-1} respectively.

Table 11: Adsorption of Cd^{2+}, $Ni2^{+}$, and Pb^{2+} onto NaOH TSG at uniform conditions of PH, contact time, initial metal ion concentration and adsorbent dosage.

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent(g)	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	2.85	0.495	0.908
Ci-Ce	47.1	49.5	49.1
%MR=Ci-Ce/Ci*100	94.3	99.0	98.2
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	9.43	9.90	9.82

Table 12: Adsorption of Cd^{2+},Ni^{2+}, and Pb^{2+} onto NH_4Cl Treated Spent Grains at uniform conditions of pH, contact time, initial metal ion concentration and adsorbent dosage

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	9.73	3.12	2.36
Ci-Ce	40.3	46.9	47.6
%MR=Ci-Ce/Ci*100	80.5	93.8	95.3
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	8.05	9.38	9.53

Table 13: Adsorption of Cd^{2+},Ni^{2+}, and Pb^{2+} onto NaCl Treated Spent Grains at uniform conditions of pH, contact time, initial metal ion concentration and adsorbent dosage

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	3.14	0.905	1.69
Ci-Ce	46.9	49.1	48.3
%MR=Ci-Ce/Ci*100	93.7	98.2	96.6
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	9.37	9.82	9.66

Table 14: Adsorption of Cd^{2+},Ni^{2+}, and Pb^{2+} onto Na_2CO_3 Treated Spent Grains at uniform conditions of pH, contact time, initial metal ion concentration and adsorbent dosage

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	1.74	1.42	2.50
Ci-Ce	48.3	48.6	47.5
%MR=Ci-Ce/Ci*100	96.5	97.2	95.0
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	9.65	9.72	9.50

Table 15: Adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} onto H_2SO_4 + NaOH Treated Spent Grain at uniform conditions of PH, contact time, initial metal ion concentration and adsorbent dosage

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	9.28	4.83	1.56
Ci-Ce	40.7	45.2	48.4
%MR=Ci-Ce/Ci*100	81.4	90.3	96.9
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	8.14	9.03	9.69

Table 16: Adsorption of Cd^{2+}, Ni^{2+}, and Pb^{2+} onto Citric acid + NaCl Treated Spent Grain at uniform conditions of PH, contact time, initial metal ion concentration and adsorbent dosage

	Cd^{2+}	Ni^{2+}	Pb^{2+}
Mass of adsorbent	1	1	1
Temperature(°C)	27	27	27
pH	10	10	10
Time(mins)	60	60	60
Ci(mg/L)	50	50	50
Ce(mg/L)	9.68	3.48	1.80
Ci-Ce	40.3	46.5	48.2
%MR=Ci-Ce/Ci*100	80.6	93.1	96.4
Vol. of solution(L)	0.2	0.2	0.2
Qe=(Ci-Ce)v/m	8.06	9.31	9.64

Conclusion

Brewery spent grains, a cheap, an environmentally friendly and a readily available low-cost adsorbent was successfully utilized for the removal of Pb (II) , Ni(II) and Cd(II) ions from aqueous solution by batch adsorption method. In the same vein, several adsorbents prepared from the brewery spent grains by modification with various reagents demonstrated an excellent sorbent property for the adsorption of lead, nickel and cadmium from aqueous systems. Excellent sorbent properties were observed when sorption studies were conducted for the removal of Cd^{2+}, Ni^{2+}, and Pb^{2+} using different adsorbents, namely sodium hydroxide treated spent grains (NaOH TSG), sodium chloride treated spent grains (NaCl TSG), sulphuric acid and sodium hydroxide treated spent grains (H_2SO_4 + NaOH TSG), sodium chloride + Citric acid treated spent grains (NaCl + $C_6H_8O_7$ TSG), sodium carbonate treated spent grains (Na_2CO_3 TSG), ammonium chloride treated spent grains (NH_4Cl TSG) and unmodified brewery spent grains. Sodium hydroxide treated spent grains had the highest metal efficiency removal for Ni^{2+} and Pb^{2+}while sodium carbonate treated spent grains recorded the highest metal efficiency removal for Cd^{2+}.From the results, it was found that the Nigerian Brewery wastewater in Kaduna State has significant concentrations of 1.46 mgL^{-1}, 0.756 mgL^{-1} and 0.343 mgL^{-1} for nickel, lead and cadmium respectively, with the amount of nickel in the wastewater exceeding the maximum permissible limit set by both national and international regulatory bodies, like, FEPA, USEPA and WHO.

References

[1] Akhtar, N., Syakirlshak, M.I., Bhawani, S.A. and Umar, K. (2021). **Various Natural and Anthropogenic Factors Responsible for Water Quality Degradation: A Review**. *Water,* 13(19): 2660. https://doi.org/10.3390/w13192660

[2] Zhang, S., Fu, K., Gao, S., Liang, B., Lu, J. and Fu, G. (2023). **Bioaccumulation of Heavy Metals in the Water, Sediment, and Organisms from The Sea Ranching Areas of Haizhou Bay in China.** *Water,* 15(12): 2218. https://doi.org/10.3390/w15122218

[3] Ohiagu, O.F., Chikezie, C.P., Ahaneku, C.C. and Chikezie, M.C. (2022). **Human exposure to heavy metals: toxicity and health implications.** *Material Science and Engineering International Journal,* 6(2): 78-87

[4] Imo, C.I., Nwakuba, N.R., Asoegwu, S.N. and Okereke, N.A.A. (2017). **Impact of brewery effluents on surface water quality in Nigeria: a review**. *Chemistry Research Journal*, 2(6): 101-113

[5] Iwuozor, K.O. and Emuobosa, E.G. (2018). **Physic-Chemical parameters of industrial effluents from a brewery industry in Imo State, Nigeria.** *Advanced Journal of Chemistry-Section A*, 1(2): 66-78

[6] Silva, J.A. (2023). **Wastewater Treatment and Reuse for Sustainable Water Resources Management: A Systematic Literature Review**. *Sustainability,* 15(14): 10940. https://doi.org/10.3390/su151410940

[7] Nicula, N.O., Lungulescu, E.M., Rîmbu, G.A., Marinescu, V., Corbu, V.M. and Csutak, O. (2023). **Bioremediation of Wastewater Using Yeast Strains: An Assessment of Contaminant Removal Efficiency**. *International Journal of*

Environmental Resources and Public Health, 20(6):4795. doi: 10.3390/ijerph20064795.

[8] Carrasco, K.H., Höfgen, E.G., Brunner, D., Borchert, K.B.L., Reis, B., Steinbach, C., Mayer, M., Schwarz, S.; Glas, K. and Schwarz, D. (2022). **Removal of Iron, Manganese, Cadmium and Nickel Ions Using Brewers' spent Grain**. *Polysaccharides,* 3: 356-379.

[9] Baiano, A., la Gatta, B., Rutigliano, M. and Fiore, A. (2023). **Functional Bread Produced in a Circular Economy Perspective: The Use of Brewers' Spent Grain**. *Foods,* 12(4):834. doi: 10.3390/foods12040834.

[10] EPA (2010). **Wastewater sampling procedure**

[11] Ogbu I.C., Akpomie K.G., Osunkunle A. A, Eze S.I. (2019). **Sawdust-kaolinite composite as efficient sorbent for heavy metal ions**. *Bangladesh J. Sci. Ind. Res.* 54(1):99-110.

[12] Wyasu, G. (2020). **Determination of Physicochemical Pollutants In Wastewater and Some Food Crops Grown Along Kakuri Brewery Wastewater Channels, Kaduna State, Nigeria.** *Science World Journal*, 15(3):https://doi.org/10.47514/swj/15.03.2020.016

[13] Nnaji, C.C., Ebeagwu, C.J. and Ugwu, E.I. (2017). **Physicochemical conditions for adsorption of lead from water by rice husk ash**. *Bio Resources*, 12(1): 799-818

[14] Itodo, A.U., Gav, L.B. and Chia, M. (2023). **Adsorption removal of ampiclox from aqueous solution using treated Okobo coal**. *ChemSearch Journal,* 14(1): 76-90

[15] Devnani, B., Moran, G.C. and Grossmann, L. (2023). **Extraction, composition, functionality and utilization of brewers' spent grain protein in food formulations**. *Foods*, 12(7): 1543-1548

[16] Liu, Z., Sun, Y., Xu, X., Qu, J. and Qu, B. (2020). **Adsorption of Hg (II) in an aqueous solution by activated carbon prepared from rice husk using KOH activation**. *ACS Omega*, 5(45): 29231-29242

[17] Bashiri, S., Ghobadian, B., Soufi, M.D. and Gorjian, S. (2021). **Chemical modification of sunflower waste cooking oil for biolubricant production through exporidation reaction**. *Material Science for Energy Technology,* 4:119-127.

[18] Ezeonuegbu, B.A., Machido, D.A., Whong, C.M.Z., Japhet, W.S., Alexiou, A., Elazab, S.T., Qusty, N., Yaro, C.A. and Batiha, G.E.S. (2021). **Agricultural waste of sugarcane bagasse as efficient adsorbent for lead and nickel removal from untreated wastewater: biosorption, equilibrium, isotherm, kinetics and desorption studies**. *Biotechnology Reports*, 30,e00614.https://doi.org/10.1016/j.btre.2021.e00614.

[19] Rudi, N.N., Muhamad, M.S., TeChuan, L., Alipal, J., Omar, S., Hamidon, N., Abdul Hamid, N.H., Mohamed Sunar, N., Ali, R. and Harun, H. (2020). **Evolution of adsorption process for manganese removal in water via agricultural waste adsorbents**. *Heliyon,* 6(9):e05049.doi: 10.1016/j.heliyon.

[20] Ancuta, C. and Adriana, D. (2020). **Brewer's spent grains. Possibilities of valorisation** review. *Applied Sciences,* 10(16):5619;https://doi.org/10.3390/app10165619

[21] Mahdi, Z., Yu, M.Q. and El Hanandeh, A. (2018). **Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar**. *Journal of Environmental Chemical Engineering*, 6(1): DOI: 10.1016/j.jece.

[22] Wang, Y., Lv, Y., Shen, H., Xu, S., Guo, Y., Bao, Z. And Feng, Y. (2020). **Preparation of naoh modified spent grain absorbent and adsorptive properties for dyes. IOP conference series**: *Material Science and Engineering*, 735(1): 1-11

[23] Ashagrie, L.A., Belachew, Z.T. and Abrham, B.W. (2022). **Chemical Modification of Teff Straw Biomass for Adsorptive Removal of Cr (VI) from Aqueous Solution: Characterization, Optimization, Kinetics, and Thermodynamic Aspects**. *Adsorption Science and Technology*, 8:1-25

[24] Wassie, A.B. and Srivastava, V.C. (2016). **Chemical treatment of teff straw by sodium hydroxide, phosphoric acid and zinc chloride: adsorptive removal of chromium**. *International Journal of Environmental Science and Technology,* 13: 2415-2426

[25] Gupta, S. and Kumar, A. (2019). **Removal of nickel (II) from aqueous solution by biosorption on A. barbadensis Miller waste leaves powder**. *Applied Water Science,* 9: 96 Applied Water Science https://doi.org/10.1007/s13201-019-0973-1

[26] Luísa, P.C., Morgana, M., Bruno, E., Raquel, P. and Guiné, F. (2021). **Ideal pH for the adsorption of metal ions Cr6+ , Ni2+ , Pb2+ in aqueous solution with different adsorbent materials**. *Open Agriculture*, 6: 115–123

[27] Taylor, J.H. and Soltani, M.S. (2023). **Carbonaceous adsorbents in the removal of aquaculture pollutants: a technical review of methods and mechanisms**. *Ecotoxicology and Environmental Safety,* 226: 1-36.

[28] Ho, C., Ekemezie, P., Akpomie, K. and Olikagu, C.S. (2018). **Calcined Corncob-Kaolinite Combo as New Sorbent for Sequestration of Toxic Metal Ions from Polluted Aqua Media and Desorption**. *Frontiers in Plant Science*, 6:273.doi:10.3389/fchem.00273

[29] Kerrou, M., Bouslamti, N., Raada, A., Elanssari, A., Mrani, D. and Slimani, M.S. (2021). **The use of sugarcane bagasse to remove the organic dye from wastewater.** *International Journal of Analytical Chemistry*, 28:2021:5570806.doi:10.1155/2021/5570806

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