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RESEARCH ARTICLE

ZEOLITE MATERIALS DERIVED FROM WATER HYACINTH AND RICE HUSK ASHES CLEAR TURBIDITY AND REMOVE LEAD IONS FROM CONTAMINATED WATER

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ABSTRACT

Water hyacinth plant is known to jam water bodies with thousands of tons of floating plant matter. In order to help in its control, it is important to explore ways to create value in its products especially the ones that can find use in water remediation. On the other hand rice husk is not waste anymore for its ash is rich in active silica. Thus, the present study determined the capacity and efficiency of water hyacinth ash, its insoluble residue, and rice husk ash to remove lead ions and turbidity from contaminated water. Mixtures of the two ashes were used to prepare zeolitic materials A and B by hydrothermal reactions. Material A was prepared using rice husk ash and the soluble fraction of water hyacinth ash while for material B, a mixture of equal amounts the two ashes including the insoluble residue of water hyacinth ash were used. The efficiency of the material was investigated by varying the effect of initial lead ions concentration, pH, contact time, temperature and adsorbent dose. Adsorption data for lead ions on rice husk ash, water hyacinth ash residue and materials A and B best fitted the Langmuir model and gave adsorption capacities of 37.04, 83.33, 142.86 and 278.6 mg/g respectively while water hyacinth ash best fitted Freundlich model and gave an adsorption capacity of 61.69 mg/g. The findings herein indicate that incorporating the residue of water hyacinth ash in the synthesis of the zeolitic material enhances its adsorption capacity and efficiency for lead ions and also imparts ability to remove turbidity.

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INTRODUCTION

In Kenya where the population is estimated to be about 40 million people, 43 percent (17.2 million) has no access clean water. The major factors contributing to this water crisis include; rapid population growth, recurrent droughts, forest degradation, poor management of water supply and water contamination. This water crisis may worsen as industrial development and population grows as projected if drastic measures are not taken immediately. The rapid population growth both in rural and urban areas has stressed the existing water supply systems (Vorosmarty et al., 2000). This accompanied by unsuitable water supply infrastructure has hindered access to water by the poor in many developing countries (Rosegrant and Cai, 2002). There has been remarkable growth in light and informal (Jua Kali) industries like textiles, leather, paper, plastics,

electroplating, cement, metal processing, wood preservatives, paints, pigments and steel fabricating industries (Cheng, 2003). These industries discharge large quantities of toxic wastes (Chen et al., 2007). Recent studies in Kenya have shown that the unregulated open-air mechanical workshops are significant sources of mobile and bioavailable heavy metal contaminants (Chengo et al., 2013a, b). Several studies suggest that among the heavy metals, pollution associated with lead ions is of key concern in Kenya (Muiruri et al., 2013; Muinde et al., 2013; Nasiebanda et al., 2014) and Africa (Yoshinori et al., 2010; Akoto et al., 2008). More so because lead is a non-essential element and toxic even at very low levels of exposure. Even low doses can impair the nervous system and affect fetus, infants and young children. Low level lead exposure leads to encephalopathy, ischemic heart disease, abnormalities in children, testicular atrophy, anemia and interstitial nephritis (Tong et al., 2000). The maximum allowed levels of lead ions in drinking water is capped at 15 µg (Levin et al., 2008). Turbidity is a key physical characteristic that expresses water's optical property to scatter and absorb rather than transmit light.

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This is caused by suspended matter or impurities that may include clay, silt, microscopic inorganic and organic matter, soluble colored compounds, plankton and other microscopic organisms. Excessive turbidity in drinking water is visually unpleasant and may also symbolize a health concern. Turbidity promotes growth of pathogens in water systems leading to waterborne disease outbreaks. Although it is not a direct indicator of health risk, many studies have shown correlation between removal of turbidity and removal of protozoa (Herson *et al.*, 1984; Gauthier *et al.*, 2003). Several processes used to remove turbidity and dissolved heavy metals include ion exchange, precipitation, ultra filtration, reverse osmosis, electro dialysis and adsorption (Tchobanglous and Burton, 1991). Many of these approaches demand high energy, advanced operational requirement or difficult to treat and do not enable recovery of metals or material.

Water hyacinth is one of the most stubborn weeds of the world (Gopal and Sharma, 1981). Water hyacinth infestations are symptoms of eutrophication. Indeed studies have identified high concentrations of nutrient in water as the overriding factor affecting growth parameters of water hyacinth plants. Work done by Coetzee *et al.*, 2007 established that the growth rate of water hyacinth leaves and daughter plants at high concentrations levels was more than double their production at low concentrations. At high nutrient levels, the plant promptly covers water bodies and surrounding marshy regions at an average growth of one ton of dry matter per day per hectare (Mailu, 2001). Consequently such colonized wetlands decline in the quantity and quality of water they provide (Wilson *et al.*, 2005). This affects aquatic ecosystems health and the biodiversity of the water bodies (Greenfield *et al.*, 2007).

Due to increased contamination of the already scarce clean water, there is need to explore ways of developing relatively simple and cheap water filtration materials that can be used at household level for its remediation. In an attempt to develop cheap adsorbents using water hyacinth as one of the raw material as a means of aiding incurring or putting it under maintained control, the present work aimed at developing adsorbents from water hyacinth and rice husk waste. Indeed findings herein suggest that water hyacinth and rice husk waste can be used as raw materials for synthesizing adsorbent materials for heavy metal removal from contaminated water. This work was done between the months of October 2012 to September 2013 at Kenyatta University, Chemistry department, research laboratory.

MATERIALS AND METHODS

Chemicals: The stock solutions of lead with a concentration of 1000 mg/L were prepared by dissolving 1.600 g lead nitrate in 1000 mL distilled water in volumetric flask. The solution was then diluted to obtain standard solutions containing 0.1 mg/L, 0.2 mg/L, 0.4 mg/L, 0.8 mg/L, 1.6 mg/L 3.2 mg/L. Nitric acid and sodium hydroxide solutions were used in all experiments to adjust pH of the solution.

Rice husk ash, water hyacinth ash and water hyacinth ash residue preparation: Water hyacinth plants were obtained from Nairobi dam. They were then transported to the laboratory where they were extensively washed with tap water to remove soil and dust, sliced into pieces and then air dried for one week using a procedure already documented by

(Kruatrachue *et al.*, 2004). Ashing was done using an oven at a temperature of 950 °C for 5 hours. The resulting ash was mixed to obtain a composite water hyacinth ash, WHA. Samples were sieved to obtain particles of the same size. Water hyacinth ash residue, WHAR was obtained after 50 g of water hyacinth ash were dissolved in 250 cm³ of distilled water, shaken for five minutes and allowed to settle. Filtration was done using Whatman No.1 filter paper and the residue was sun dried for five hours. Rice husks were provided by Euros rice millers in Kirinyaga County, Mwea west district. They were then washed several times with distilled water to remove soil and dust, followed by filtration and then dried at 100 °C. The clean and dry rice husks were burnt in an oven at 500 °C for 3 hours to obtain rice husk ash, RHA.

Potassium hydroxide solution: 1M potassium hydroxide was generated from water hyacinth ash by dissolving 50 g of WHA and filtering off the residue. Titration experiments were done to determine the concentration of the alkaline solution using 0.1M hydrochloric acid.

Synthesis of zeolitic material, ZMA: About 25 g of rice husk ash was put into a stainless steel digestion bomb. A 250 mL potassium hydroxide solution was added to the ash. The bomb was closed and introduced into a pre-heated oven at 200 °C for a period of 24 hrs. The contents were then allowed to cool and filtered. The solid residue was then washed with distilled water to remove the excess alkali and dried at 105 °C for 12 hrs. The solid residue was designated as ZMA.

Preparation of zeolitic material B, ZMB: For the preparation of ZMB, 50 g of rice husk ash and 50 g of water hyacinth ash were put in a digestion bomb and 250 mL of distilled water added to the mixture. The bomb was put in a pre-heated oven at 200 °C for 12 hours. The resultant solid was washed with hot distilled water to remove the excess alkali and then dried at 105 °C for 12 hrs. The sample was designated as ZMB.

Instrumentation: Lead concentrations in the various solutions were determined using atomic absorption spectrophotometer model AAS 4141, ECIL, India at wave length 283.3 nm in flame mode using air-acetylene flame. The pH meter, model PHEP, Hanna instrument, Italy, was used in this study between pH ranges 2-12 at a temperature of 22.7 °C. Turbid meter, model 2100P (HACH) was used to determine the turbidity of water. The concentration of the Pb²⁺ was assayed in triplicates by use of an AAS with air-acetylene flame. The accuracy of the instrument was checked by triplication of samples. A series of standards were prepared for instrumental calibration by serial dilution of a working solution (100 mg/L) they were prepared from analytical grade stock solution (1000 mg/L) from Alpha Chemika and S.D. Fine-chem ltd. A standard and blank sample was run after every seven samples to check instrumental drift. Calibration curve method was used to quantify the heavy metal concentration.

Batch experiments: In the batch experiments a water-bath temperature controlled shaker (DKZ-1 NO.1007827) was used for the batch adsorption study. The experiments were performed at a constant shaking speed. For each experimental run, 50 mL aqueous solution of the known concentration of lead solution was taken in 120 mL plastic bottles containing a known mass of the adsorbent. These bottles were agitated at a constant shaking rate of 150 rpm in a temperature of 25 °C. 0.1 g of RHA, ZMA, ZMB, WHA and WHAR were used for

adsorption of Pb^{2+} . Triplicate solutions and 100 mg/L Pb^{2+} ion solutions was mixed with 0.1 g of adsorbent and shaken for 24 hours at a temperature of 25 °C, centrifuged and filtered. The concentrations of Pb^{2+} ions in the resultant filtrates were measured using flame atomic absorption spectrometry. The amount and percentage of Pb^{2+} ions adsorbed were calculated using the equation 1 and 2 respectively

$$qe = \frac{(C_0 - C_e)}{m} V \rightarrow \quad (1)$$

$$R = 100 \left(\frac{C_0 - C_e}{C_0} \right) \rightarrow \quad (2)$$

Where, qe = Amount of metal ion removed at equilibrium

C_0 = Initial concentration of sorbate

C_e = Concentration of sorbate at equilibrium

m = mass of adsorbent used

V = volume of solution used

Effect of adsorbent dosage: The effect of adsorbent dosage on the percentage of Pb^{2+} ions adsorbed was investigated by agitating Pb^{2+} solutions at various dosages ranging from 0.02 to 2.5 g at fixed contact time, initial metal ion concentration and pH. Initial concentrations of the aqueous metal solution of Pb^{2+} were kept constant at 10 mg/L for WHA, RHA and ZMA and 100 mg/L for WHAR and ZMB. The initial pH of each metal ion solutions was adjusted to its respective optimum pH. The experiment was conducted in triplicates and agitated for 2 hrs on the water bath shaker. At the end of the contact time, the samples were centrifuged and filtered using Whatman No.1 and Pb^{2+} concentrations of the filtrates determined using flame atomic adsorption spectrometry.

Effect of contact time: The percentage of Pb^{2+} ions adsorbed at various contact time was investigated using 50 mL of 10 mg/L sample solutions in eight plastic bottles. 0.1 g of WHA, RHA and ZMA were added to each bottle. The concentrations were adjusted to 100 mg/L for WHAR and ZMB. The pH of the sample solutions were adjusted to 5. The bottles were shaken at 120 rpm for times ranging from 1min to 24 hrs. The solutions were then filtered and the filtrates were subjected to atomic absorption to record the absorbance of lead and determine concentrations of Pb^{2+} ions.

Effect of initial concentration of Pb^{2+} ions: The effect of initial concentration of Pb^{2+} ions on the percentage of Pb^{2+} adsorbed was investigated by agitating 50 mL samples of leads solutions of 10 mg/L in 120 mL plastic bottles with 0.1 g of ZMA, WHA and RHA adsorbents in a water bath shaker at 25°C. Pb^{2+} ion concentrations were adjusted to 100 mg/L for WHAR and ZMB. The contact time was kept constant at 2 hours and initial pH of solution set at 5 using sodium hydroxide solution and nitric acid. Samples were withdrawn after 2 hours, filtered using Whatman No. 1 and measured for Pb^{2+} ion concentrations. All tests were conducted in triplicate.

Effect of pH: The effect of pH on the percentage of Pb^{2+} ions adsorbed was studied by varying the pH from 2 to 12. The adjustments were done using concentrated nitric acid and concentrated sodium hydroxide solution. 0.1 g of RHA, WHA and ZMB were added to 50 mL aqueous solutions containing 10 mg/L lead ions. The concentrations of lead solutions were adjusted to 100 mg/L for WHAR and ZMB. All tests were conducted in triplicates.

The samples were agitated using the water shaker at constant speed of 150 rpm and contact time of 2 hours. At the end of the contact time, the samples were filtered using Whatman No.1 and the concentrations of Pb^{2+} ions in the filtrates determined using flame atomic absorption spectrometry.

Suspended particles in water: Turbid water was prepared by adding clay materials to tap water. About 25 g of the clay materials was added to 1 litre of tap water. The suspension was stirred for about 1 hour to achieve a uniform dispersion of clay particles. Then it was allowed to settle for at least 24 hours for complete hydration of the clay material. The effect of doses of WHA, RHA, WHAR, ZMA and ZMB was investigated by agitating 50 mL of turbid water with 0.1, 0.2, 0.3, 0.4, and 0.5 g of adsorbents for 2 hrs. The solution was then filtered using Whatman No. 1 filter paper and turbidity of the filtrate determined using a turbid meter. All these studies were conducted at room temperature and at a constant speed of 150 rpm.

RESULTS AND DISCUSSION

Characterization of Materials: The XRD scattering pattern of ZMA is shown in figure 1 and its subsequent theoretical phase chemical composition given in table 1. As shown, all the zeolites contained aluminosilicates minerals similar to those of naturally occurring zeolites. ZMA which was synthesized from RHA and the soluble part of WHA gave phase matches shown in table 1. The matches indicate that the material comprises of a zeolite framework mainly neutralized by Fe ions along Mg and Ca ions. This agrees with XRF data of ZMA presented in table 2. As shown the percentage oxides in descending order were SiO_2 , Fe_2O_3 , Al_2O_3 , K_2O , CaO , TiO_2 and MgO at 75, 10.45, 7.8, 3.3, 1.1, 1.3 and 0.45 % composition respectively. Fig 2 shows the XRD scattering pattern of ZMB which was synthesized from RHA and WHA including the insoluble portion. The pattern was almost identical to the one for ZMA suggesting that the structures were very similar. However, phase matches indicated that the material comprises of a zeolite framework mainly neutralized by Mg and Ca ions. In addition phase matches of aluminum phosphate and iron silicide were obtained as shown in table 3. This concurs well with XRF data of the percentage oxides in descending percentage composition of 76.22, 10.52, 4.63, 2.7, 2.08, 2.01, 1.76 and 0.04 % for SiO_2 , Al_2O_3 , P_2O_5 , K_2O , MgO , Fe_2O_3 , CaO and TiO_2 respectively as indicated in table 4.

Effects of initial metal concentration: Figure 3 shows how the percentage of Pb^{2+} ions adsorbed at saturation varied as the initial concentrations were varied from 10 to 100 mg/L for RHA and ZMA and 100 to 500 mg/L for WHA, WHAR and ZMB when 0.1 g of adsorbents were used under same conditions. Variation of the initial concentration from 100 to 500 mg/L decreased the % removal by ZMB from 99 ± 12.6 to 75 ± 9.6 %. The percentage removal by WHAR increased as the concentration increased from 100 mg/L to 300 mg/L. Further increase in concentration decreased the percentage removal to 99.2 ± 0.6 % at 500 mg/L. The high and gradual increase in the percentage removal of lead ions as initial concentration increases for WHAR suggest it has large number of active sites and equilibrium constant, (K_{eq}) than the others. The decrease indicates that saturation of active adsorption sites occurs at initial concentration levels of above 300 mg/L. The percentage removal of lead ions by WHA remained unchanged as initial concentrations were increased to 500 mg/L.

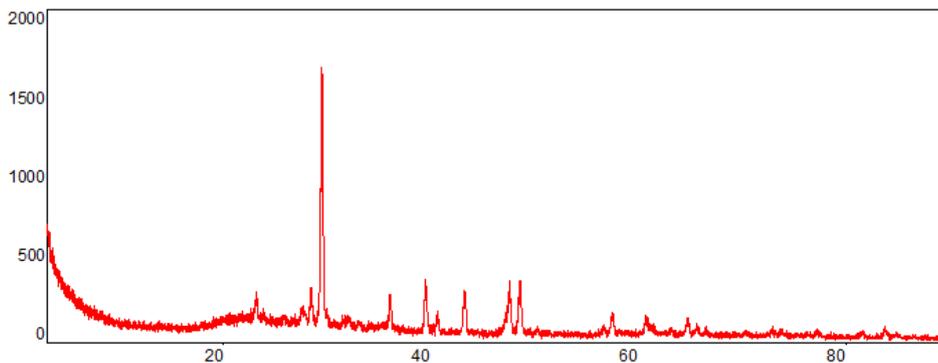


Figure 1. XRD scattering pattern for material ZMA

Table 1. Phase matches for XRD scattering pattern of material ZMA

Phase name	Mineral	% content
Magnesioferrite	Aluminosilicate	83.48915
Iron silicon oxide	Aluminosilicate	4.704745
Magnesium Iron AluminiumOxide	Aluminosilicate	9.212560
Zeolite 4A	Aluminosilicate	2.593544

Table 1. XRF percentage oxides data of material ZMA

Compound	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MgO	Fe ₂ O ₃
% oxide	7.8%	75%	3.3%	1.1%	1.3%	0.45%	10.45%

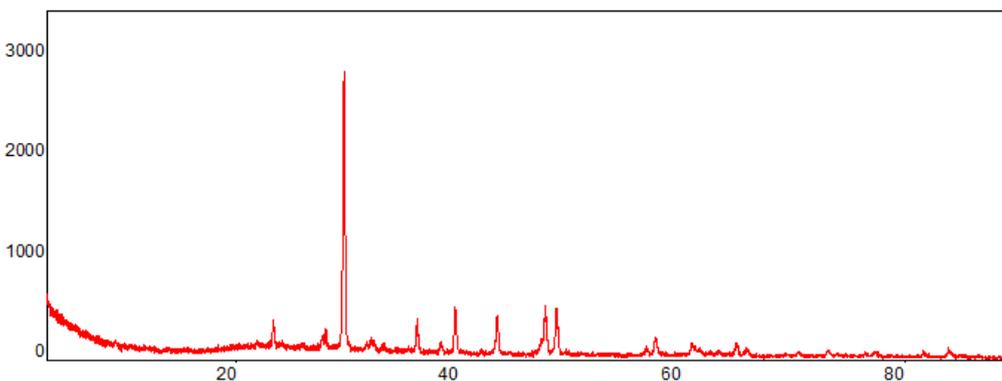


Figure 2. XRD scattering pattern for material ZMB

Table 3. Phase matches for XRD scattering pattern of material ZMB

Phase name	Mineral	Content (%)
Magnesium catena-silicate, clinoenstatite	Aluminosilicate	81.4908
Aluminum phosphate(V)	Silicoaluminophosphate	4.157738
Iron silicide	Aluminosilicate	14.174103
Zeolite 4A	Aluminosilicate	0.177361

Table 4. XRF percentage oxides data of material ZMA

Compound	Al ₂ O ₃	SiO ₂	K ₂ O	CaO	TiO ₂	MgO	Fe ₂ O ₃	P ₂ O ₅
% oxide	10.52%	76.22%	2.7%	1.76%	0.04%	2.08%	2.01%	4.63%

Table 3. Thermodynamic data for Pb²⁺ from Langmuir and Freundlich adsorption isotherms

sample	Langmuir			Freundlich		
	q _{max} ,mg/g	b dm ³ /g	R ²	1/n	K _f ,mg/g	R ²
RHA	37.04	0.22	0.997	0.393	9.33	0.925
WHA	20.40	0.65	0.724	3.779	61.69	0.768
WHAR	333.3	0.5	0.959	0.253	177.01	0.953
ZMA	83.33	46.83	0.996	0.393	9.33	0.182
ZMB	142.86	0.293	0.983	0.182	66.07	0.767

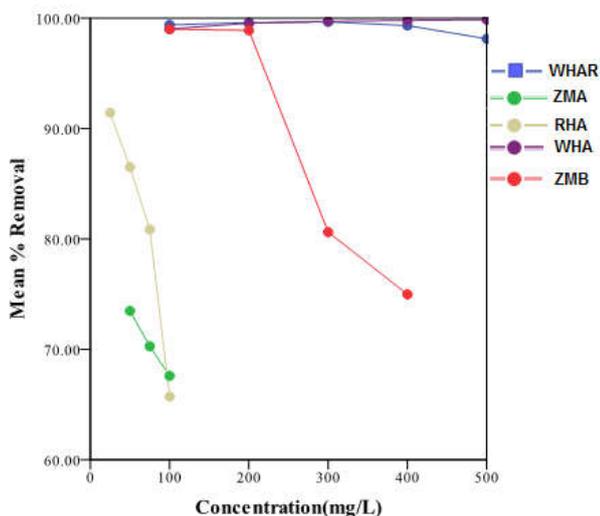


Figure 3. The percentage removal of Pb²⁺ at saturation using 0.1g of water hyacinth ash, rice husk ash and zeolite at various initial concentrations (amount of biosorbent = 0.1 g, contact time = 24 hours and agitation speed = 120rpm)

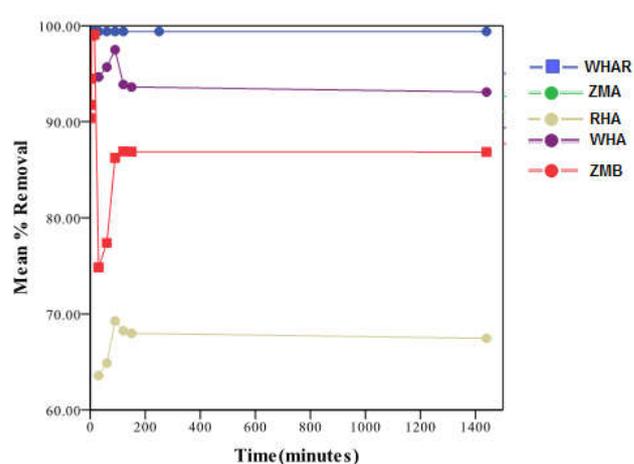


Figure 6. Effect of contact time on the adsorption of Pb²⁺ at pH 5.0, agitation speed 120 rpm, temperature 25 °C and initial metal ion concentration of 10mg/L for RHA, WHA and ZMA and 100mg/L for WHAR and ZMB

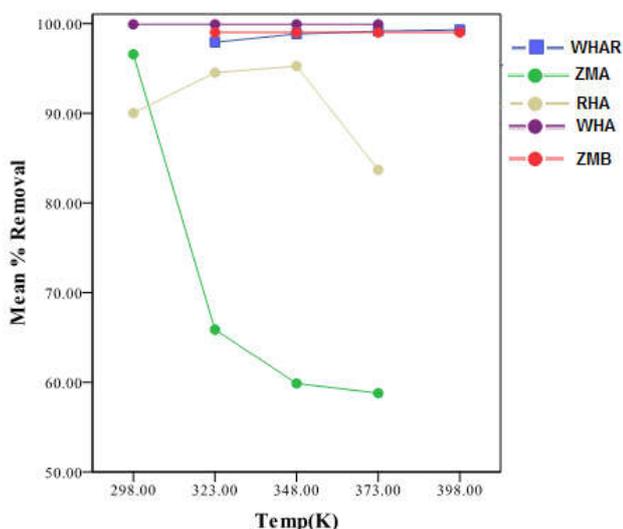


Figure 4. Effect of temperature on the removal of Pb²⁺ by water hyacinth ash, rice husk ash and zeolite (initial solution concentration = 10 mg/L for RHA, WHA and ZMA and 100mg/L for WHAR and ZMB, amount of biosorbent = 0.1 g and contact time = 120 min agitation speed = 120rpm)

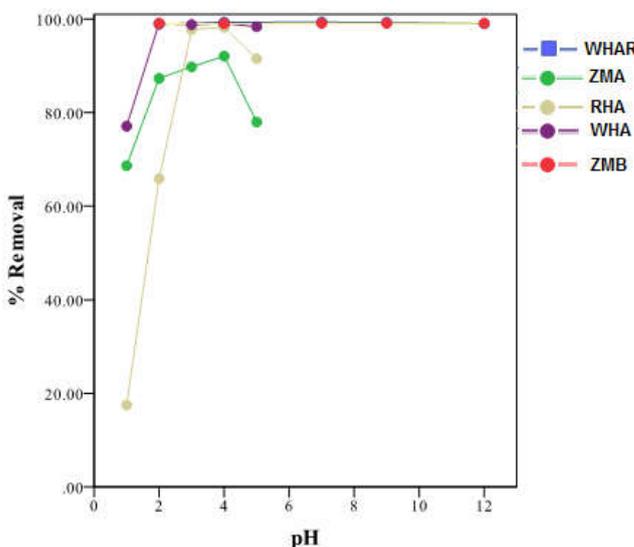


Figure 7. Effect of pH on the adsorption of Pb²⁺ using 0.1g of adsorbent at contact time 2 hours, agitation speed 120 rpm, temperature 25 °C and initial metal ion concentration of 10mg/L for RHA, WHA and ZMA and 100mg/L for WHAR and ZMB

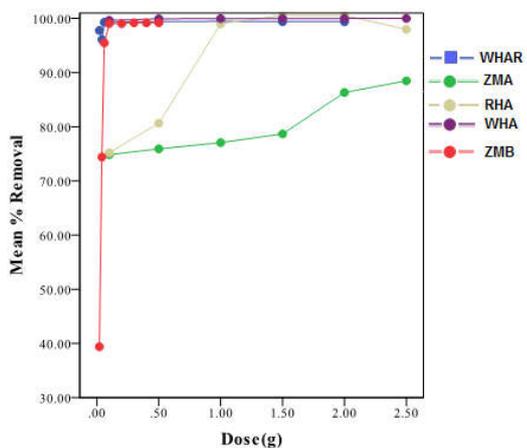


Figure 5: Effect of adsorbent dosage (g) variation on Pb²⁺ adsorption at pH of 6, agitation period of 120 min at 120 rpm and initial metal ion concentration of 10mg/L for RHA, WHA and ZMA and 100mg/L for WHAR and ZMB

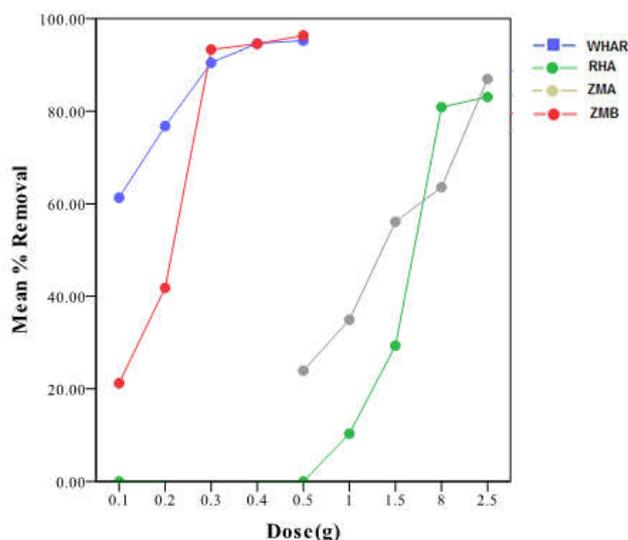


Figure 8. Removal of suspended particles from water using different adsorbent dosages and agitation period of 120min at 120rpm, Temperature 25°C for WHAR, RHA, ZMA and ZMB

However, since WHA contains 35.8 ± 0.1 % K_2O , it is possible that precipitation of Pb^{2+} ions at the higher pH contributed to the high percentage removal. The percentage removal of Pb^{2+} ions by rice husk ash reduced drastically from 93 ± 12.8 to 65 ± 8.9 % as concentration increased from 10 mg/L to 100 mg/L. In ZMA, a gradual decrease of percentage removal as initial concentration was varied from 10, 25, 50, 75 and 100 mg/L was observed. The decrease is so gradual that variation of initial concentrations from 10 to 75 ($7\frac{1}{2}$ times) corresponds to a decrease in percentage removal from about 75 ± 3.1 % to about 71 ± 2.9 %, indicating that all the number of binding sites decreased with increase in concentration of the Pb^{2+} ions.

Effects of temperature: The variations of percentage removal of lead ions adsorbed by WHA, WHAR, RHA, ZMA and ZMB were investigated as a function of temperature and the observations summarized in figure 4. The experiments were done at temperatures of 25, 50, 75, 100 and 125 °C using doses of 0.1 g / 50 mL, pH of 6 and initial concentrations of 10 mg/L for RHA, WHA and ZMA while initial concentration of 100 mg/L was used for WHAR and ZMB. The percentage removal of Pb^{2+} ions by water hyacinth ash residual, WHAR increased from 97.00 ± 0.61 % to 99.30 ± 0.63 % when the temperature was increased from 50 to 125 °C. Percentage removal of lead ions by RHA increased from 90.01 ± 5.27 % to 95.25 ± 5.57 % when the temperature was increased from 25 to 75 °C. Thereafter, the concentration of lead ions removed by RHA decreased to 83.67 ± 4.91 %. This implies that at temperatures above 75 °C, the Pb^{2+} ions possess sufficient energy to overcome the enthalpy of adsorption on RHA. Percentages of Pb^{2+} ions removed by ZMA gradual decreased from 96.56 ± 2.44 to 58.78 ± 1.49 % when the temperature was increased from 25 to 100 °C suggesting that the ions are weakly held. The percentage removal of Pb^{2+} ions by ZMB and WHA remained constant with increase in temperature suggesting that ZMB and WHA Pb^{2+} adsorption was not affected by increase in temperature.

Effect of adsorbent dosage: Figure 5 shows how the percentage removal of Pb^{2+} ions varied as adsorbent doses were increased from 0.02 to 2.5 g. The experiments were done at pH of 6, agitation period of 120 min at 120 rpm and initial metal ion concentration of 10 mg/L for RHA, WHA and ZMA and 100 mg/L for WHAR and ZMB. The results showed that as the adsorbent doses were increased, the percentage removal of Pb^{2+} ions increased for all the five adsorbents. A gradual increment in percentage removal of 10 mg/L metal ion concentration by RHA was recorded as doses were increased from 0.1 to 0.5 g and a steeper one between 0.5 to 1 g. This plateaued between 1 and 2 g and decreased at 2.5 g. Reduction in capacity is due to overlapping of adsorption sites as a result of overcrowding of adsorbent particles as reported by Tumin *et al.*, 2008 leading to a concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Moreover, a high adsorbent dosage could impose a screening effect on the dense outer layer of the cells, thereby shielding the binding sites from metals (Bishnoi *et al.*, 2004). For ZMA, a gradual increase in percentage removal of Pb^{2+} ions was recorded at 0.1 and 1.5 g and a steeper one beyond 1.5 g. There was no significant change in the amount of lead ions adsorbed as the doses of WHA was increased. A rapid increments in the percentage removal of Pb^{2+} ions by ZMB and WHAR were observed as their doses were increased from 0.02 g to 0.06 g and then remained

constant beyond 0.1 g. The initial increment in percentage adsorption with increments in adsorbent dosage was due to increments in available adsorption sites for metal attachment (Abdel *et al.*, 2007).

Effect of contact time: The variations of percentage removal of Pb^{2+} ions as contact time was increased to 24 hours as represented in Figure 6. The percentage of the adsorbed Pb^{2+} ions increased as the time increased similar to literature reports (Meena *et al.*, 2005). RHA showed gradual increment of adsorbed Pb^{2+} ions in the first 30 min followed by a rapid metal ion adsorption for the first 60 min. This was followed by a gradual decrease beyond 60 min and remained constant beyond 150 min. The percentage removal by WHAR and ZMB remained constant beyond 30 and 15 min respectively. The fast adsorption at the initial stage was probably due to the initial concentration gradient between the adsorbate in solution and the number of vacant sites available on the surface at the beginning. The progressive increase in adsorption and consequently the attainment of equilibrium was due to limited mass transfer of the adsorbate molecules from the bulk liquid to the external surface of the adsorbents.

Effects of pH: The effects of pH on the percentage removal of Pb^{2+} ions by the various adsorbents are represented in figure 7. As observed from figure, RHA performs its best between pH 7-9 at percent removal of close to 100. ZMA gave best percentage removals of 83-86 % at pH values of between 4 and 9 while WHA performed best above pH values 4. The percentage removal of Pb^{2+} ions by WHAR and ZMB remained fairly constant as the PH was increased from 2 to 12 with percentage removal of close to 100.00 ± 0.01 %. At low pH (< 4), there was excessive protonation of the active sites at the adsorbents surface and this hinders the formation of bonds between Pb^{2+} ions and the active site. Further increase in pH above 4 led to decreased adsorption of Pb^{2+} ions by ZMA and RHA. At pH 7-9, removal of the lead ions remained almost constant in all the five adsorbents. At moderate pH values, linked H^+ is released from the active sites and adsorbed amount of metal ions is found to increase. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption as observed (Olayinka *et al.*, 2009). Removal of metal ions at higher pH values could be attributed to the formation of their hydroxides which results in precipitates, this is consistent with the observation of Lisa *et al.*, 2004. Therefore, removal of Pb^{2+} ions at higher pH values may be due to the formation of precipitates rather than adsorption. (Patnukao *et al.*, 2008) concluded that adsorption experiments for Pb^{2+} ions are better performed at moderate pH to avoid precipitate formation. Decrease in adsorption at higher pH (> 7) is associated to the formation of soluble hydroxyl complexes (Amuda *et al.*, 2007).

Percentage removal of suspended particles: The percentage of turbidity removed in different adsorbent dosages by water hyacinth ash residue, rice husk ash water hyacinth ash and ZMB, in different dosages is described in Figure above. The highest removal was indicated at adsorbent dosage 0.5 g water hyacinth ash residue with removal efficiency of 95.0 ± 2.1 %, 0.5 g ZMB with removal efficiency of 96.0 ± 2.2 %, 2.5 g, rice husk ash with removal efficiency of 83.0 ± 1.9 % and 2.5 g water hyacinth ash with removal efficiency of 86.0 ± 2.0 % while the minimum removal was 0.0 ± 0.0 % recorded at 0.1 g and 0.5 g rice husk ash, 61.0 ± 2.8 % at 0.1 g water hyacinth ash residue, 21.0 ± 0.9 % at 0.1 g ZMB and 23.0 ± 0.5 % at 0.5 g

water hyacinth ash. The removal efficiency remained fairly constant when the adsorbent dosage was increased above 0.4 g ZMB, 0.4 g water hyacinth ash, 2.0 g rice husk ash and 2.0 g water hyacinth ash.

Adsorption isotherms: The data obtained from the batch adsorption experiments were fitted to Langmuir and Freundlich isotherms at a constant temperature of 25 °C and important thermodynamic data obtained as shown in Table 3.

As implied by R^2 values of 0.997, 1, 0.996 and 0.983 and $1/n$ values of less than one for RHA, WHAR, ZMA and ZMB respectively, the data best fits into Langmuir isotherm model. This indicates a monolayer sorption onto adsorbent surfaces that contain finite number of identical active sites. The adsorption capacities of the adsorbents, q_{max} were 37.04 ± 0.18 , 278.60 ± 3.66 , and 83.33 ± 0.86 and 142.86 ± 1.48 mg/g for RHA, WHAR, ZMA and ZMB respectively. WHAR gave the highest adsorption capacity of 278.6 ± 3.66 mg/g, a value close to the one reported for nanocrystalline zeolite of 270.27 mg/g (Muhammad and Munawar, 2007). This is despite that it contains 54.8 % of CaO which is likely to cause water hardness. ZMA had an adsorption capacity of 83.33 mg/g, a value higher than the one obtained for natural zeolite tuff in single and binary systems of 68 mg/g (Wang *et al.*, 2008) and montmorillonite-illite type clay of about 52 mg/g (Oubagaranadin and Murthy, 2009). The adsorption capacity of ZMB was found to be 142.86 ± 1.48 mg/g which is about twice the value reported for natural zeolite. This value is much higher than most values reported for bio-sorbents (Saeueprasearsit *et al.*, 2010) and activated carbon (Lalhruaitluanga *et al.*, 2009) The adsorption data for WHA best fitted into Freundlich isotherm as indicated by the R^2 value of 0.772 versus Langmuir's value of 0.732. Its adsorption capacity, K_f , and $1/n$ values were 61.69 ± 0.81 mg/g and 3.78 ± 0.05 respectively. The $1/n$ value of greater than 1 indicates cooperative adsorption thus supporting that precipitation of Pb^{2+} ions at basic conditions brought about by WHA may be contributing to precipitation of Pb^{2+} ions.

Conclusion

This study shows that WHA and RHA can be used to produce zeolitic materials which are good adsorbents for Pb^{2+} and suspended particles removal from water. Biosorption in RHA, WHAR, ZMA and ZMB are best described by monolayer Langmuir isotherm model WHAR and ZMB gave the highest q_{max} of 278.6 ± 3.66 mg/g and 142.86 ± 1.48 mg/g respectively. These findings imply that incorporating the water hyacinth ash residue into the zeolitic material enhances adsorption of Pb^{2+} ions and also imparts ability to remove turbidity.

Conflict of Interests: The authors declare that there is no conflict of interests regarding the publication of this paper.

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