REMOVAL OF HEAVY METAL IONS FROM AQUEOUS SOLUTION USING RICE HUSKS-BASED ADSORBENTS

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ABSTRACT

This study reports on the preparation and characterization of rice husks-based adsorbents and their application in the removal of heavy metal ions from aqueous solution. Three different adsorbents were developed: rice husks ash (RHA), rice husks ash-derived silica (RHS) and triaminopropyl-silica hybrid (TSH-R). The prepared materials were characterized by acid titration, Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy, Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX) spectroscopy and nitrogen physisorption analysis. Results from the ATR-FTIR analysis indicated that pure silica was obtained from RHA and that after surface modification the triaminopropyl group was successfully attached onto the silica framework with a loading of 2.15 mmol per g silica. The RHA, RHS, TSH-R had average particle sizes of 336.8, 296.4 and 1054.1 nm and BET surface areas of 17.8, 20.2 and 5.7 m^2*/g, in the same order. Adsorption studies of* Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} *and* Co^{2+} *ions showed that RHA and TSH-R were good adsorbents with an average maximum adsorption of 99 and 95 % for RHA and TSH-R, respectively when 1.0 g of adsorbent and initial metal ions concentration of 21 - 27 mg/L at pH 4 were employed. Both Langmuir and Freundlich isotherms indicated that the adsorption was favorable.*

Key Words: Triaminopropyl-silica hybrids, rice husks ash, rice husks silica, adsorption

INTRODUCTION

Most heavy metal ions such as Ni^{2+} Zn^{2+} Pb^{2+} Cu^{2+} and Co^{2+} are toxic and can exist for a long time in the environment. These metals cause serious environmental and public health problems even at very low concentrations (Yu *et al*. 2011). The heavy metal ions are normally discharged from nuclear, metallurgical, tannery, mining, cosmetics, insecticides, photography, textiles, paints, dyes and battery industries (Wang *et al*. 2012). Production of these toxic heavy metals has attracted close attention all over the world due to the metals environmental persistency and toxicity. They do accumulate in water bodies as well as in the food chain (Gupta *et al*. 2013). Generally, toxic heavy metals have been reported to cause potential human health risk and ecological disturbances (Han *et al*. 2012).

For environmental and public health safety, different conventional physico-chemical methods have been deployed to remove toxic heavy metals from waste water. Such methods include ion exchange, reverse osmosis, electrochemical precipitation, electro-dialysis, evaporation and solvent extraction (Rohaizer *et al*. 2013). However, these methods are capital intensive in terms of operational and maintenance costs (Bhattacharya *et al*. 2006). Recent studies, however, show that adsorption is one of the most cost effective and versatile methods for removal of heavy metals from aqueous media (Okoye and Obi 2012, Gervas *et al*. 2015).

Various adsorbent materials such as activated carbon, zeolites, clays and mesoporous silicas are capable of capturing metal ions from dilute aqueous solution. It has been shown that functionalized mesoporous silica with a high density of amino groups and well-defined meso-channels that can enhance the accessibilities of molecules can efficiently adsorb heavy metal ions such as Pb^{2+}, Cu^{2+}, Cd^{2+} and Cr^{2+} (Chen *et al*. 2012). Different optimization approaches have been used to improve the adsorption capacity of the mesoporous silica. They include surface functionalization with various organic moieties as well as incorporation of heteroatoms such as Al, Ti, Zr, into the silica framework (Rohaizer *et al*. 2013). Currently, research efforts have shifted towards the development of new, low cost adsorbents preferably from biogenic sources. An adsorbent may be regarded as low cost if it is abundant in nature, is a by-product, a waste material from industry or requires little processing. In this study, locally available agricultural waste (i.e., rice husk) was utilized in the developing adsorbents for removal of heavy metal ions from aqueous solution.

MATERIALS AND METHODS

Materials and Reagents

Rice husks were obtained from Ulanga, Morogoro, Tanzania, (3-trimethoxysilylpropyl) diethylenetriamine, (assay 97%) was purchased from Sigma Aldrich-UK and other standard laboratory reagents were purchased from LOBA CHEMIE PVT LTD. All chemicals were used as received.

Extraction of Silica from Rice Husks Ash

Rice husks ash (RHA) was obtained by burning rice husks in a high temperature muffle furnace (Model F46120CM) at 650 ºC for 8 hours. Silica was extracted by using a method adapted from previous studies (Awizar *et al*. 2013). In a typical procedure, pure silica was obtained by dissolving 10 g portions of RHA in 200 mL of 2 M NaOH solution, boiled for 1 hour and allowed to cool to room temperature. The mixture was filtered using Whatman No. 41 filter paper to obtain sodium silicate, discarding the residues. Thereafter 2 M HCl were added to the filtrate to precipitate silica. The obtained precipitates were filtered using a vacuum filtration pump followed by washing and drying in an oven for 36 hours at 90 ºC to get pure silica**.**

Analysis of Selected Heavy Metal Ions in Silica Prepared from Rice Husks Ash

Analysis of Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+}, Cr^{2+} and Co^{2+} in the silica extracted from RHA was done using Atomic Absorption Spectroscopy (AAS). A sample solution was prepared by wet digestion method. In a typical procedure 1.00 g of silica was dissolved into 50 mL *aqua regia* followed by dilution with distilled water to 250 mL. Thereafter the solution was filtered and analyzed by Atomic Absorption Spectrophotometry (AAS).

Preparation of Triaminopropyl-silica Hybrids

The triaminopropyl-silica hybrids (TSH-R) were synthesized by a post synthetic technique using the RHA-derived silica as described elsewhere (Macquarrie *et al*. 1997). A typical procedure involved air-drying the silica at 120 ºC for 24 hours, followed by mixing 10 g of the dried silica and 5.37 g of (3-trimethoxysilylpropyl) diethylenetriamine in a 100 cm^3 round-bottomed flask containing 50 cm^3 of toluene. The mixture was then stirred and refluxed for 16 hours after which the solid materials were filtered and washed thoroughly with toluene, dichloromethane and acetone successively. The resultant material was first dried in air at room temperature and then temperature raised to 120 ºC.

Characterization of the Triaminopropyl-silica hybrids

Acid titration was done to determine the amount of surface bound species (loading) whereas attenuated total reflectance infrared (ATR-FTIR) spectroscopy was used to ascertain the functional groups present on the surface of the prepared material. The morphology and elemental composition of the materials were determined by Scanning Electron Microscopy coupled with Energy Dispersive X-ray spectrometry (SEM-EDS). The porosity properties were studied using nitrogen physisorption analysis.

Metal Ions Adsorption Experiments

Batch adsorption tests were carried out to determine the capacity of the adsorbents in removing metal ions from aqueous solutions. The study was conducted using a single metal ion solution (*viz*. Pb^{2+} solution) or a solution containing a mixture of metal ions, *viz*. Cu^{2+}, Co^{2+}, Pb^{2+} and Zn^{2+}.

The adsorption experiments were carried out at 28 ºC using solution concentrations ranging from 20 to 60 mg/L maintained at pH 5.3. In a typical procedure 1.0 g of adsorbent were put in different round bottomed flasks containing 50 mL of a known concentration of metal ion/mixture of metal ions. The solutions were agitated at 200 rpm for 60 minutes using a Digital Grant Bio Shaker HY-51 machine. The solutions were then filtered using Whatman No. 41 filter paper. The initial and equilibrium metal ion concentrations were analyzed by using AAS.

RESULTS AND DISCUSSION

Extraction and characterization of silica from rice husks ash

Extraction of pure silica from RHA gave a yield up to 90%, results that are comparable with those reported elsewhere (Thuadaij and Nuntiya 2008, Santasnachok *et al*. 2015). Figure 1 shows the products that were obtained at different stages during the extraction process.

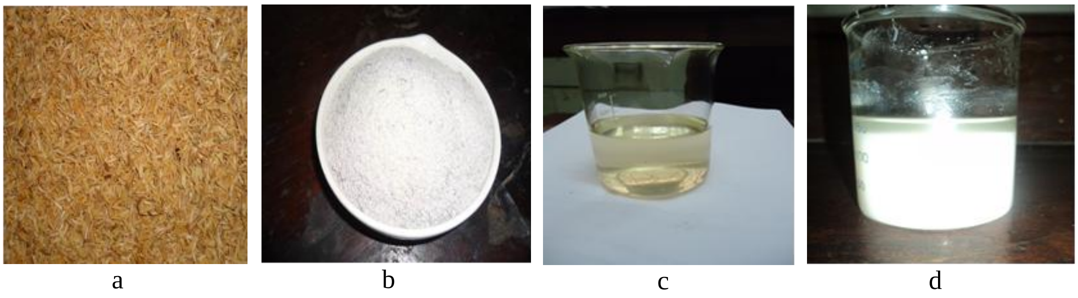

Figure 1: Pictures showing (a) raw rice husks (b) rice husks ash (c) Na_2SiO_3 solution and (d) white silica precipitates.

The obtained silica had functional groups similar to commercial silica as determined using IR spectra (Figure 2). The spectra show a wide O-H stretching band between 3000 and 3500 cm^{-1} due to freely vibrating OH groups and a band at 1600-1650 cm^{-1} attributable to O-H bending vibration (Abdel

Rahim *et al*. 2015**)**. The peak at around 1100 cm^{-1} and 967 cm^{-1} are due to Si–O-Si asymmetric stretching and Si–OH stretching vibrations, respectively.

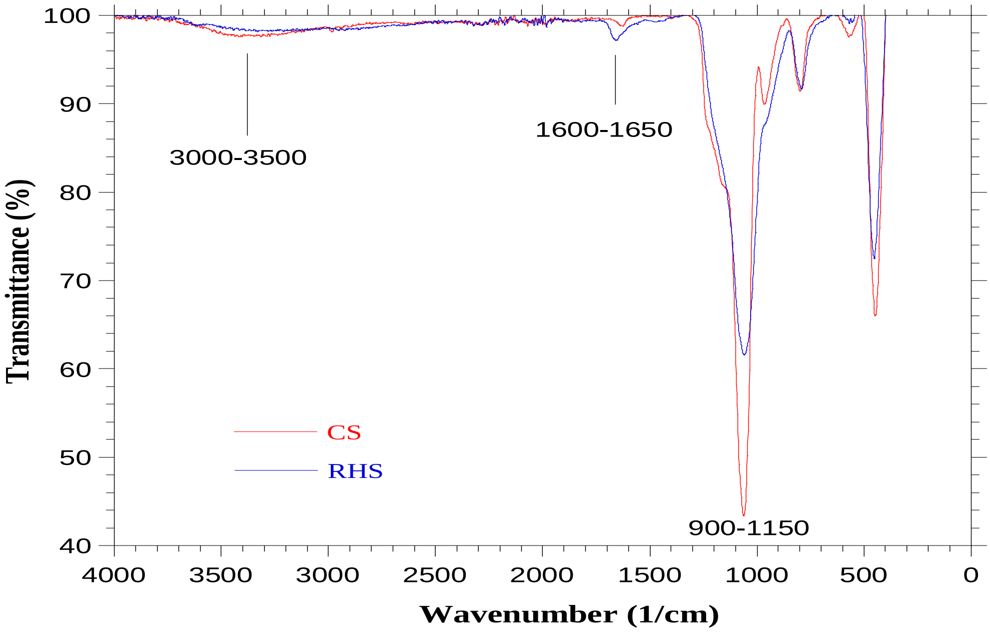

Figure 2: ATR-IR spectra for commercial silica (CS) and RHS.

In addition, the spectra also show peaks at 819 cm^{-1} and 441 cm^{-1} which are due to Si–O–Si symmetric stretching and bending vibrations. The absence of peaks at 2800 and 3000 cm^{-1} indicates that there were no organic compounds in the extracted silica.

Since the RHA-derived silica were to be developed to an adsorbent for heavy metal ions, it was prudent to establish whether it contained or not any metal ions prior to its application. In that case analysis of Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} and Cr^{2+} ions was conducted using AAS. The results are given in Table 1. As observed from the table, the extracted silica did not contain the studied heavy metals except for traces of copper and cobalt. The trace amounts of copper and cobalt could be impurities, which might have been introduced during the handling of the waste rice husks. The observed concentrations were, however, very small to have any significant effect on the adsorption measurements.

Table 1: Concentration of heavy metal ions in silica prepared from RHA

Heavy metal ion	Ni(II)	Zn(II)	Pb(II)	Cu(II)	Cr(II)	Co(II)
Concentration (mg/L)	BD L	0.32	BDL	0.08	0.02	0.10

BDL= below detection limit

Functionalization of the extracted silica with (3-trimethoxysilylpropyl) diethylenetriamine afforded an organo-silica hybrid with amino functional groups. Acid titration indicated that the amino group loading was 2.15 mmol/g silica. The presence of amino groups in the hybrid material was important for its application as an adsorbent. The tethering of the organic groups onto the silica frameworks was confirmed by IR analysis. The IR spectrum of the TSH-R showed new peaks for alkyl CH_{st} (2800-3000 cm^{-1}) and N-H bending (1530 cm^{-1}) in addition to the peaks for silica, results that confirm that indeed the organic group was on the silica framework (Figure 3).

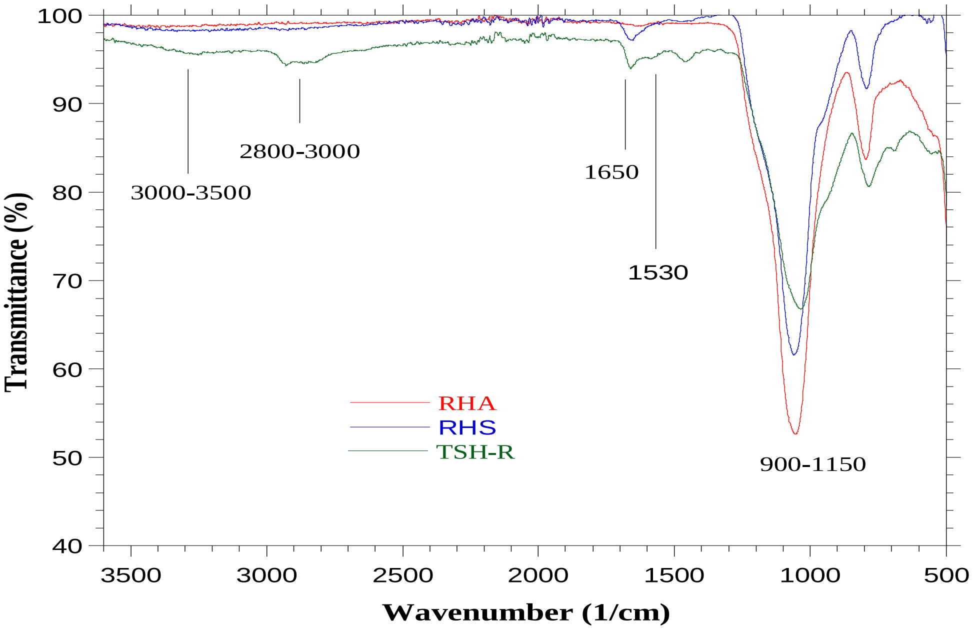

Figure 3: ATR-IR spectrum for RHA, RHS and TSH-R superimposed

The porosity characteristics of RHA, RHS and TSH-R were studied using BET nitrogen physisorption at -196.15°C. The adsorption-desorption isotherms for RHA, RHS and TSH-R of type IV as typified by the adsorption-desorption isotherm for TSH-R in Figure 4. The isotherm has two inflation points due nitrogen uptakes; the first is slow at low relative pressure (< 0.1) and the second is sharp at relative pressure of about 0.95 with a hysteresis loop at a relative pressure above 0.6. The higher nitrogen uptake at low relative pressure is indicative of monolayer adsorption whereas the sharp uptake at a higher relative pressure shows multilayer adsorption (Rouquerol and Sing, 1999).

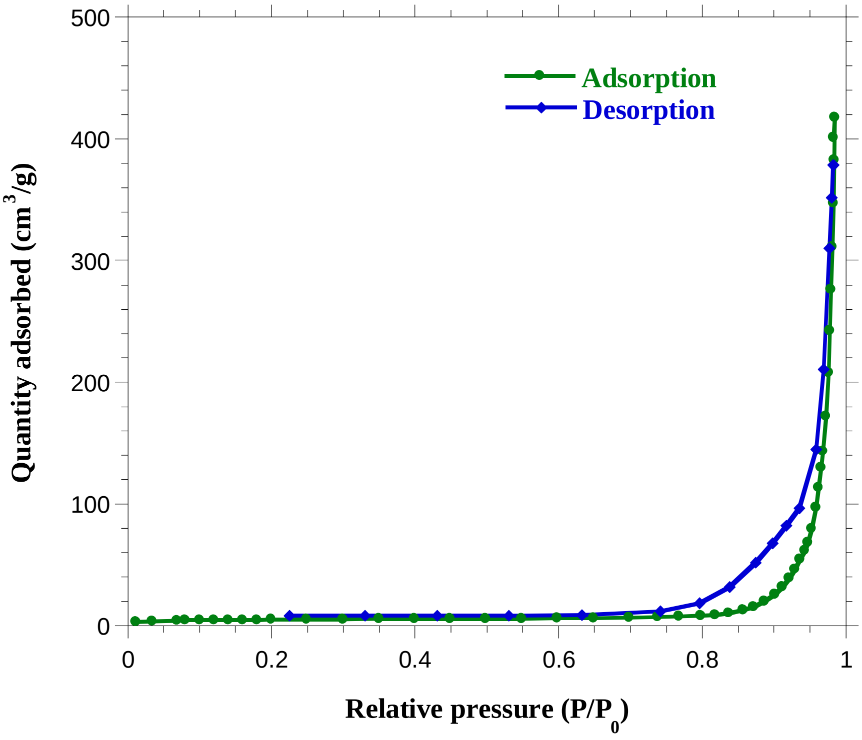

Figure 4: Adsorption-desorption isotherm of TSH-R

The porosity properties of the RHA, RHS and TSH-R were determined by the analysis of nitrogen adsorption-desorption isotherms using the BET method. Table 2 gives a summary of the BET surface areas, pore volumes, average pore diameters and particle sizes of these materials. As seen from the table the surface areas of RHA and RHS were almost similar, with that of RHS being slightly high. This also applies to their pore diameters. The pore diameters were 95.9 and 97.6 nm for the RHA and RHS, respectively.

Table 2: Physicochemical properties of RHA, RHS and TSH-R

Sample	Average pore width (nm)	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average particle size (nm)
RHA	95.9	17	0.43	336
RHS	97.6	20	0.49	296
TSH-R	17.3	6	0.02	1054

The low surface areas and large pore diameters is an indication that the materials are non porous and that porosity that is accounted for by the adsorption data is probably the void spaces between particles. In addition, the particle sizes for the materials were 336 and 296 nm for the RHA and RHS, respectively. Upon derivatisation of the RHS with (3-trimethoxysilylpropyl) diethylenetriamine, the particles merged and the size increased to 1054 nm. The derivatisation also led to a drastic drop in surface area, pore size and pore volume (Table 2). The observed decrease is probably not only due to the merging of the particles but also due to steric effects caused by the attachment of functional groups which protruded into the void spaces thereby decreasing the adsorption of the nitrogen gas. The merging of the particles is clearly seen in the SEM micrographs given in Figure 5. From the figure it is seen that the RHA has irregular particles that are loosely packed. On the other hand, the RHS particles are slightly compact, but they retain the irregular shapes. When derivatisation takes place, the particles increase in size, forming agglomerates.

Elemental composition data as determined by SEM-EDX is given Table 3. The results show that in general RHA and RHS contain high proportions of silicon and oxygen. The data further show that RHA has a small amount of carbon. This probably comes from unburnt organic material in the ash. RHA did not contain sodium or chlorine, though the same were found in RHS as well as TSH-R. The observed sodium and chlorine were a result of pH adjustment during silica extraction in which NaOH and HCl were used.

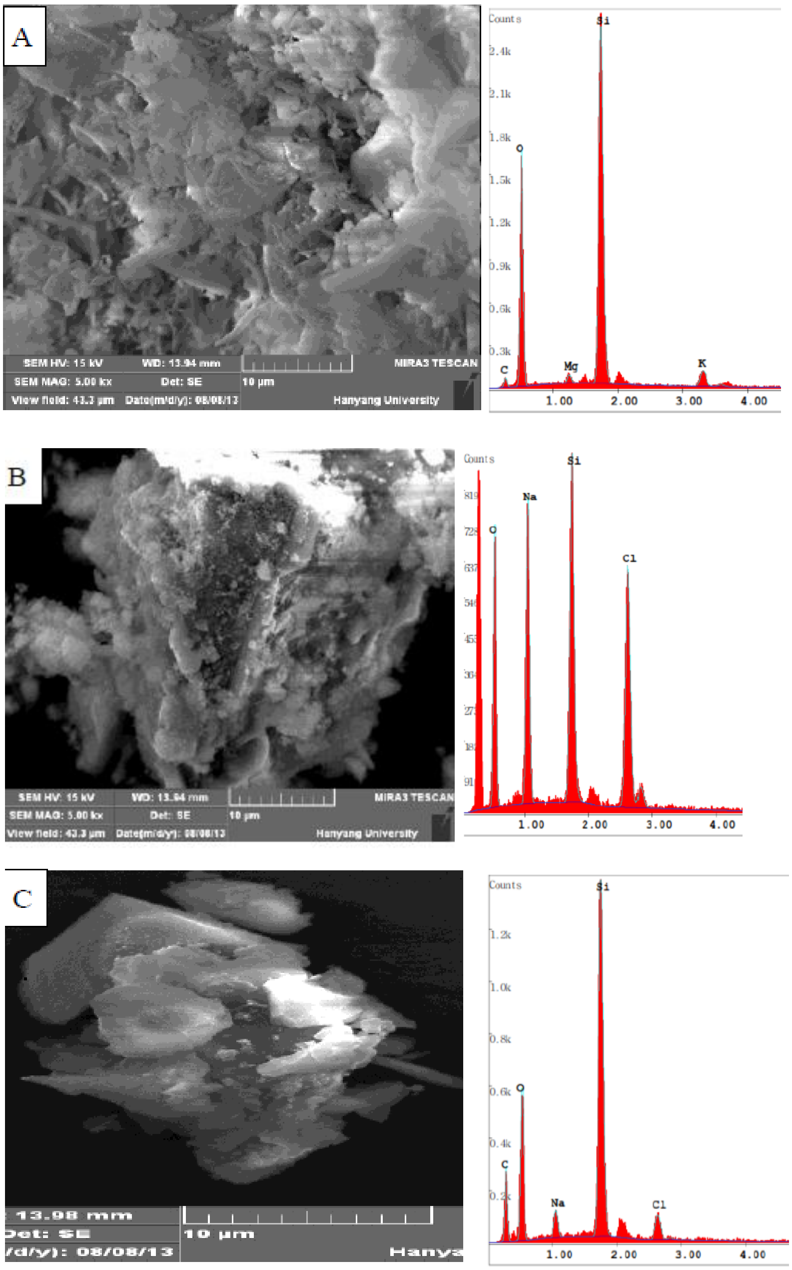

Figure 5: SEM micrographs and EDX spectra for A) RH, B) RHS and C) TSH-R

Table 3: Elemental composition of RHA, RHS and TSH-R

Element	RHA		RHS		TSH-R	
	Wt %	At %	Wt %	At %	Wt %	At %
Si	47.71	34.84	25	41.99	37.27	23.41
O	41.55	53.26	28.79	41.99	26.07	28.75
Na	-	-	18.86	19.14	2.60	1.99
Cl	-	-	26.89	17.70	4.30	2.14
Mg	1.03	0.87	-	-	-	-
K	4.69	2.46	-	-	-	-
C	5.02	8.58	-	-	29.76	43.71

Wt % = weight percent, At % = atomic percent

Adsorption of metal ions from aqueous solution

Adsorption studies were carried out to determine the capacity of RHA, RHS and TSH-R in removing heavy metal ions from an aqueous mixture of Cu^{2+}, Zn^{2+}, Pb^{2+} and Co^{2+} ions. A 1.0 g sample of adsorbent was mixed with 50 mL of an aqueous mixture of the metal ions at an initial concentration range of 21-27 mg/l. The mixtures were agitated for 60 minutes, filtered and analyzed by AAS. The results of the percentage removal are presented in Figure 6. As seen from figure 6, all three materials were capable of removing the selected heavy metal ions from an aqueous solution. RHA seemed to have the best capacity followed closely by RHS, whereas TSH-R had the least removal capacity. The differences in the adsorption capacities could be associated with their surface areas. It should be noted that RHA has the largest surface area compared to the other two adsorbents (Table 2). Surface area is an important factor for adsorption because when it is large the number of active sites also increases.

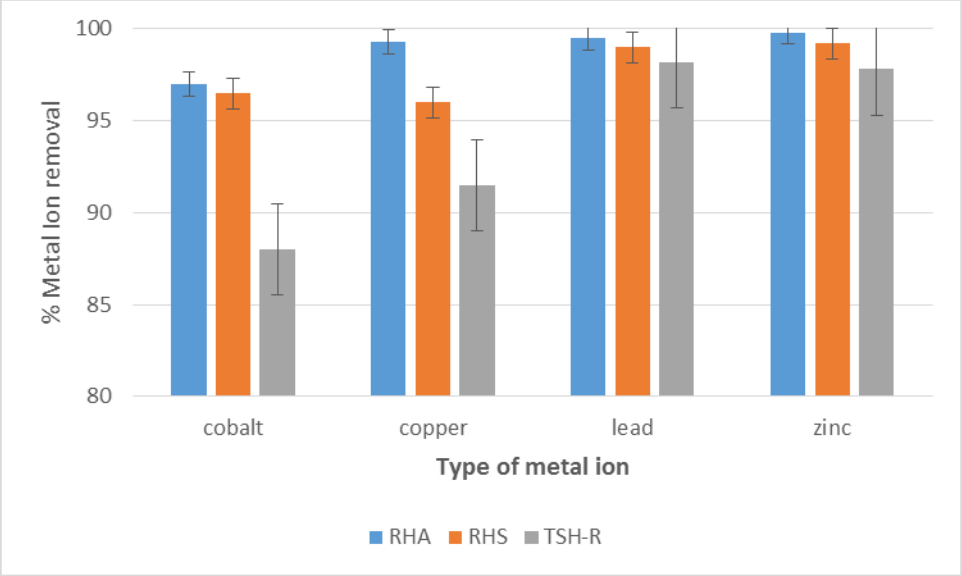

Figure 6: Adsorption of Co^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+} ions on RHA, RHS and TSH-R

Adsorption isotherm study

Adsorption isotherms normally describe the distribution of adsorbate species among liquid phase and adsorbed phase, based on the heterogeneity or homogeneity nature of adsorbents, type of coverage and an interaction between the adsorbate species. Adsorption data are usually described by adsorption isotherms, such as Langmuir and Freundlich isotherms. These isotherms relate metal uptake per unit mass of an adsorbent, q_e, to the equilibrium adsorbate concentration in the bulk fluid phase, C_e.

The Langmuir and Freundlich isothermal models were used to describe the adsorption data of lead (II) ions from aqueous solution using the prepared TSH-R at the concentration range of 19.6 mg/L to 59.0 mg/L. The Langmuir model is based on the assumption that the maximum adsorption occurs when a saturated monolayer of solute molecules is present on the adsorbent surface, the energy of adsorption is constant and there is no migration of adsorbate species on the surface plane (Bhattacharya *et al*. 2006). A linear form of the Langmuir isotherm (Equation 1) was used fit the adsorption data (Figure 7).

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (1)$$

where, C_e, q_e, q_m and b represent the equilibrium concentration of Pb(II)), adsorption capacity at equilibrium, maximum adsorption capacity and energy constant related to the heat of adsorption (Langmuir constant), respectively.

Figure 7 shows that the equilibrium data fit well to the Langmuir equation (correlation coefficient, R^2 =0.89) for the Pb(II) adsorption. From the plot the values of q_m and b were found to be 2.42 mg/g and 0.52 L/mg, respectively. The adsorption data were also used to calculate the separation factor or equilibrium parameter R_L using equation 2.

$$R_L = \frac{1}{1+bC_o} \qquad (2)$$

where, C_o is the highest initial Pb(II) ion concentration and b (L/mg) is the Langmuir constant. Usually the R_L value indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In this study the value R_L was found to be 0.031, showing that the adsorption was favorable (Bhattacharya *et al*. 2006).

The Freundlich model was also used to fit the adsorption data. A linear form of the Freundlich isotherm equation (3) was used to find the Freundlich constants K_f and n which are indicators of adsorption capacity and intensity, respectively. In this study the values of K_f and n were found to be 6.15 and 1.31, respectively, as obtained from the intercept and slope of a plot of log(C_e) vs log(q_e) (Figure 8). As seen, the value of $n > 1$ indicating that the process is favourable (Sivakumar, 2015).

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (3)$$

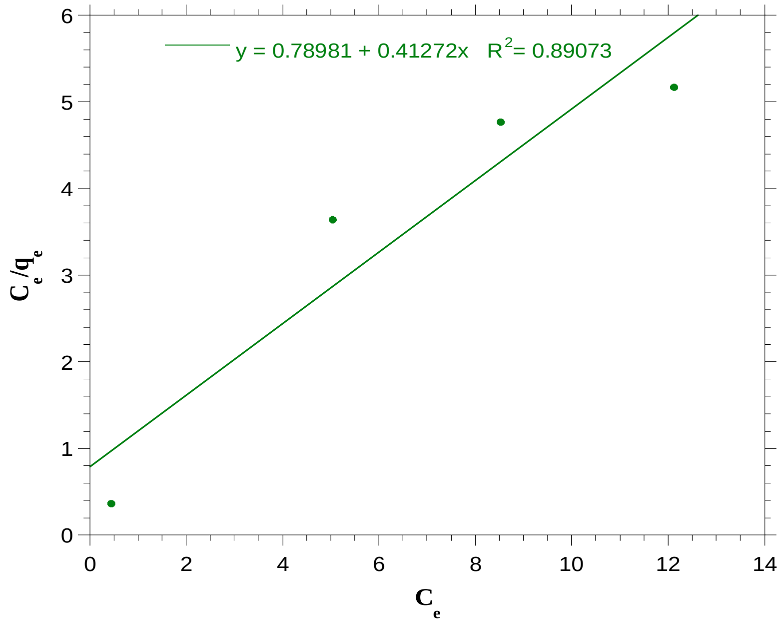

Figure 7: Langmuir adsorption isotherm for lead (II) ions on TSH-R

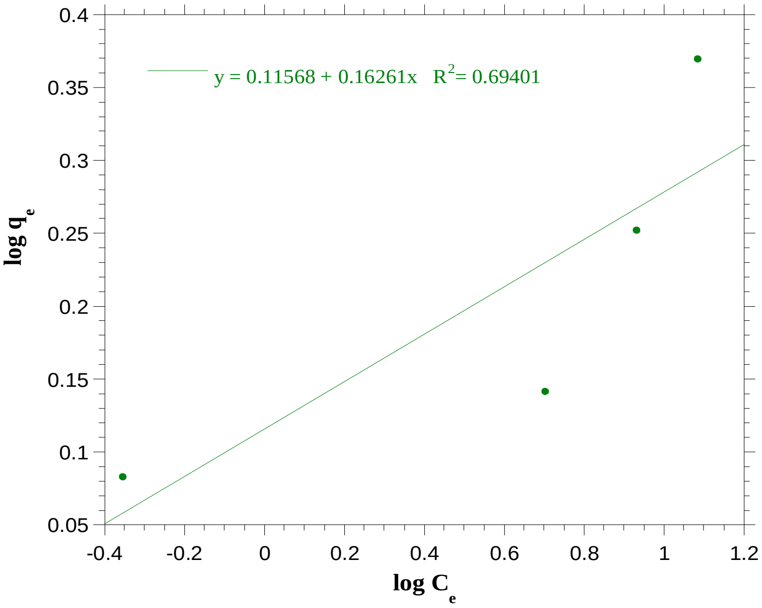

Figure 8: Freundlich adsorption isotherm for lead (II) ions on TSH-R

CONCLUSION

Rice husks-based adsorbents which are rice husks ash (RHA), rice husks ash-derived silica (RHS) and triaminopropyl-silica hybrid (TSH-R), were prepared, characterized and used in the removal of heavy metal ions from aqueous solution. The characterization of the materials indicated that they were all non porous, with an average surface area not more than 20 m^2/g. However, adsorption studies showed the materials can remove metal ions (Ni^{2+}, Zn^{2+}, Pb^{2+}, Cu^{2+} and Co^{2+}) from aqueous solution. However, their capacities varied from one adsorbent to another depending on their surface areas. RHA seemed to have the best capacity followed closely by RHS, whereas TSH-R had the least removal capacity. Both Langmuir and Freundlich isotherms indicated that the adsorption process was favorable.

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