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Adsorption Potentials of Rice Husk for Treatment of Tannery Effluent in Zaria, Nigeria

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Abstract: Chromium rich tannery effluent is a serious threat to environment that need urgent and low cost Agro-based adsorbents for removal of heavy metals. The prepared adsorbent was characterized based on the moisture content, bulk density, surface area, point of zero charge, zeta potential, fourier transform infrared (FTIR) spectroscopy, surface morphology using scanning electron microscopy (SEM), electron dispersive spectrum (EDS), and thermos-gravimetric analysis (TGA). The experiment was conducted at room temperature and adsorbent particle size of 0.15 mm to investigate the adsorption capacities of rice husk powder on removal of Cr, Cd and Cu from tannery wastewater. The experiments were conducted to evaluate the influence of variables on removal of the heavy metals by optimizing adsorbents dosage of 5, 10, 15g and contact time of 60, 120, 180 min. The results obtained from the characterization of the adsorbents indicated that the prepared bio-sorbents have good adsorptive properties with as much as 973m^2/g for rice husk surface area respectively. The bulk density; 0.386g/cm^3, moisture content; 1%, point of zero charge; 5.92, Surface area; 973m^2/g and surface morphology properties showed them to be good adsorbents. The use of rice husk mixture in the treatment of tannery effluent, indicated that rice husk is more effective in removing chromium from tannery effluent with a success of 88.6 %. Optimum operating conditions are concluded to be a contact time of 60 minutes at an adsorbent dosage of 5 g at ambient room temperature. Experimental data has well fitted into Freundlich isotherm model with R^2 value of 0.9573 and second-order kinetic model suggesting second-order nature of the process with R^2 value of 0.988, clearly indicating that one metal ion is absorbed onto two sorption sites on the adsorbent surface.

Key words: Adsorbent, Heavy metals, Leather, Wastewater

Introduction

Tanning is the chemical process that converts animal hides and skin into leather and related products. The transformation of hides into leather is usually done by means of tanning agents and the process generates highly turbid, colored and foul smell wastewater.

The tanning industry plays an important role with respect to environmental pollution due to disposal of large volume of solutions of tanning baths. More than one hundred different chemicals and nearly 350,000 tones/year of inorganic and heavy metal salts, soaps, oils, waxes, solvents, and dyes, used in tanning processes are found in process wastes and wastewater (Fabianil *et al*., 1996). The major components of the effluent include sulfide, chromium, volatile organic compounds, large quantities of solid waste, suspended solids like animal hair and trimmings. The discharge of chromium rich tannery effluent is a serious threat for environment with high concentrations of organic and inorganic component that they create risk to human health and environmental aspects (Cetin *et al*., 2013).

Many investigators have examined a wide variety of absorbents like fly-ash, peat, sawdust, brown coal, bagasse, activated carbon to remove chromium from tannery industry wastewater. Recently, numerous approaches have been studied for the development of cheaper and more effective technologies, both to decrease the amount of wastewater produced and to improve the quality of the treated effluent. Adsorption has become one of the alternative treatments, in recent years; the search for low-cost adsorbents that have metal-binding capacities has intensified (Leung *et al*., 2000). The adsorbents may be of mineral, organic or biological origin, zeolites, industrial byproducts, agricultural wastes, biomass, and polymeric materials (Kurniawan *et al*., 2005). Rice husk is one of the main agricultural wastes in milling processes that is abundantly available in Nigeria. Rice husk is an agro-waste which is produced in about 100 million of tons. About 10^8 tons of rice husks are generated annually in the world. In Nigeria about 2.0 million tons of rice is produced annually (Oyetola and Abdullahi, 2006). Approximately, 20 kg of rice husk are obtained from 100 kg of rice by burning so as to generate rice husk powder which is rich in silica and can be an economically valuable raw material for production of natural silica (Kalapathy et al. 2000). Industrial importance of rice husk (RH) is due to the presence of silica in hydrated amorphous form. The rice husk contains 80 per cent organic volatile materials and remaining 20 per cent silica (James and Subbarao, 1996).

In recent years, attention has been focused on the utilization of unmodified or modified rice husk as an adsorbent for the removal of pollutants. Batch studies using tartaric acid modified rice husk as adsorbent have been carried out for the removal of lead and copper and have reported the effects of various parameters such as pH, initial concentration of adsorbent, particle size and temperature. It was reported that modified rice husk is a potentially useful material for the removal of Cu and Pb from aqueous solutions (Wong et al., 2003). Thus, it becomes essential to remove Cr (VI) from industrial waste water before discharging it into water body or on to land (Macchi *et al*, 1991). The Nigerian Institute of Leather Technology carries out tanning process as part of its learning teaching processes and discharges the effluent into the river without proper treatment. The receiving water body either surface or groundwater get contaminated as most of the residences uses shallow wells as source of domestic water supply. In recent years, the need for safe and economical methods for the elimination of heavy metals from contaminated waters has necessitated research interest towards the production of low cost alternatives to commercially available activated carbon. Therefore, there is an urgent need that all possible sources of agro-based inexpensive adsorbents should be explored and their feasibility for the removal of heavy metals should be studied in detail. Conservative technologies for metal control have an increasing interest, as they are able to remove pollutants and reuse valuable by-products resulting from the wastes and or side streams from manufacturing processes. The objective of this study is to evaluate the adsorption kinetics and equilibrium sorption of Chromium, Cadmium and Copper to rice husk powder as adsorbents.

Materials and Method

Study area

The Nigerian Institute of Leather technology is located in Samaru Zaria, which lies within latitudes 11^0 06˝ N and 11^0 12˝ N of the equator and longitude 7^0 39˝ E and 7^0 45˝ E of the Greenwich meridian. The mean daily temperature ranged from 26.7^0C to 28.9^0C. The average duration of sunshine in August varies from 3 to 6 hours. The Galma river is the only perennial river in the area, the others are either completely dried up during the dry season along their channels. River Galma, which is also among the major tributaries of River Kaduna is the main drainage system in Zaria, supplied with run-off and seepage from drainage basin about 5.0km^2 in area (Folorunsho and Brinemigha, 2011). The estimated population of Samaru was 124,582 people (NPC, 2009). The residence of Samaru mainly depend on shallow wells (Folorunsho and Brinemigha, 2011). On the Normality of Monthly Rainfall Series of Samaru, Zaria (1979-2009). The annual average rainfall of Zaria is 1050 mm according to Köppen-Geiger system.

Preparation of the adsorbents

The preparation of the adsorbents started with the collection of Rice husk from local rice milling centre in Zaria city and mixed to form homogeneous mixture. Then, homogeneous mixture of rice husk was thoroughly washed with distilled water to clean dirt and mud and heated to the temperature of 104 °C for 3 hours. The rice husk was grinded into fine powder using kitchen grinder and sieved to particle size fraction of 100 mesh size (0.150mm).

Characterization of the adsorbents

The prepared adsorbents were characterized based on the moisture content, bulk density, surface area, point of zero charge, zeta potential, fourier transform infrared (FTIR) spectroscopy, surface morphology using scanning electron microscopy (SEM), electron dispersive spectrum (EDS), and thermos-gravimetric analysis (TGA). The determination of the adsorbent pH was carried out by using a pH meter (model ATPH-6).

Specific surface area

Saers method was used for the determination of the surface area, the volume V required to raise the pH from 4.0 to 9.0 was noted and the surface area was computed from the Equation 1:

$$s\left(\frac{m2}{g}\right) = 32v - 25 \qquad (1)$$

Where: s = surface area

v= volume required to raise the pH

m= mass of the adsorbent (g)

g= acceleration due to gravity

Moisture content

The moisture content of the adsorbents was determined by the difference in the mass constitutes of the amount of moisture content of the adsorbent, Equation 2.

$$\% \, moisture \; content = \frac{w2 - w3}{w2 - w1} \qquad (2)$$

Where: W1 = Weight of crucible

W2 = Initial weight of crucible with sample

W3 = Final weight of crucible with sample

Bulk density

The bulk density of each of the adsorbents was determined using Archimedes principle using Equation 3:

$$bulk \; density = \frac{w2 - w1}{v} \qquad (3)$$

Where: W1 = Weight of empty measuring cylinder

W2 = Weight of cylinder filled with sample

V = Volume of cylinder

Point of zero charge

pH drift method was used to determine the point of zero (PZC) charge of the adsorbents (pH pzc), a plot of final pH against initial pH gives the point of zero charge pH

Scanning electron microscopy (SEM)

The microstructures of the adsorbents (rice husk) were obtained using FE- SEM Integrated system. The samples were prepared in stub holders with double face carbon tape, placed on an aluminum sheet and covered with gold, using a Balzers SCD 050 evaporator. The same SEM samples were scanned at 100 um magnification and 20kV and the results of percentage of C, O and other metals are showed in the spectra.

Zeta potential

Zeta potential measures the electrical charges of particles that are in suspension. The zeta potential of the adsorbents (rice husk and banana peel) were obtained using a Malvern

Zetersizer Nano-ZS (Malvern, USA). The zeta potential of the sampls was then determined from their mobility based on Smoluchowski equation.

Energy-dispersive-X- ray spectrum (EDS)

The surface morphologies of the samples were characterized by scanning electron micrographs using JSM-6460LV. (Jeol) SEM. The analysis of samples was performed at various magnification sizes (50 um, 10, um, 200 nm and 500 nm) at 5-20 kV. The same SEM sample was scanned at 100 um magnification and 20kV and the results of percentage of C, O and other metals are showed in the spectra.

Fourier transform infrared (FTIR) spectroscopy

The Fourier transform analysis of the samples was performed using Thermo scientific Nicolet attenuated total reflection (ATR) instrument (6700). The samples were scanned at resolution of 4cm (32 scans) from wavelength 500 to 4000 wavelength. The software shows the spectra of sample containing peaks of different functional groups which will be used for the identification of functionalities of sample surface.

Thermo-gravimetric analysis (TGA)

The thermal behavior and decomposition pattern via thermos-grametric analysis was recorded on a TGA/DSC (SDT-Q600) analyzer by heating dry powder of the adsorbents at 10°c.

Adsorbate preparation and characterization

Physicochemical parameters including COD, BOD, DO, nitrates, phosphates, pH and metal ion concentration of the effluent sample were analyzed following standard method of water and wastewater treatment. Membrane filters of 0.45μm that were dried at 103°C for one hour, weighed and placed in a desiccator were used to determine the total suspended solids (TDS). A sterile container was used to collect the sample and mixed thoroughly by inverting the bottles several times to obtain a homogeneous mixture. Sample of 100 mL was poured into the membrane filter assembly holding the previously weighed membrane filter and attached to a suction pump and then filtered. The filter paper was then dried at 103°C and reweighed. Total suspended solids concentration was afterwards obtained by deducting the initial weight of the filter paper from its final weight. Physicochemical parameters such as nitrates, phosphates were all determined using Standard Methods for the Examination of Water and Wastewater 18th edition (APHA, 2012). The pH and temperature of the samples were analyzed using the multi-parameter photometer and thermometer respectively. The concentration of COD of respective samples was calculated using Equation 3.4:

$$\text{COD} = \frac{1000(a-b)N}{\text{volume of sample used (ml)}} \text{ mg/L} \qquad (4)$$

Where, a and b are the respective volumes of $FeSO_4(NH_4)_2SO_4.6H_2O$ used for blank and sample (ml), VIS the volume of sample used (ml) and N normality of Fe $(NH_4)_2\ 2SO_4$.

Heavy metals characterization

The heavy metals (Chromium, Cadmium and Copper) and others present in the tannery wastewater were characterized using atomic absorption spectrophotometer (AAS) Atomic absorption spectrophotometer (AAS) (Shimadzu Jenway Spectrophotometer 6400) and Atomic absorption spectrophotometer (AAS) (Shimadzu Japan Spectrophotometer AA 6800).

Batch experiment

The experiments were conducted at room temperature and adsorbents particle size of 0.15 mm to investigate the adsorption capacities of rice husk powder on removal of Cr, Cd and Cu from tannery wastewater. The experiments were conducted to evaluate the influence of variables on removal of the heavy metals by optimizing adsorbents dosage of 5, 10, 15g and contact time of 60, 120, 180 min. Tannery effluent was collected in 12 glass beakers of 50 ml capacity and was put on a mechanical shaker apparatus for different adsorbent dosage and contact time. The treated samples with various processes were filtered and the settled particles removed and collected for characterization. The clear samples after settlement (24 hours) were tested by a digital spectrophotometer to find out the reduction in concentrations of Cr, Cd and Cu in the tannery wastewater. The adsorption removal percentage was calculated using Equation 3.5.

$$\text{Percentage Removal} = [(Co-Ct) / Co \times 100] \quad (5)$$

Where: Co = Initial concentration

Ct = concentration after adsorption by adsorbent.

Isotherm and Kinetics study

For the isotherm and kinetics study, the stock solutions of Cr(VI) of concentration 500 ppm were prepared by dissolving 1.414 grams of analytical grade of $K_2 Cr_2 O_7$ in 500ml of deionized water. The stock solution is further dilute with distilled water to desired concentration for obtaining the standard solutions for absorbance measurement (Ahmed et al., 2012). The batch experiment for the isotherm study was done at room temperature to determine the equilibrium adsorption isotherms by serial dilution of the stock solution and keeping contact time constant. 5g of rice husk was added to 50ml of the stock solution and was shaken with magnetic stirrer at 250rpm for 1 hour. For the kinetic study a batch experiment was done by adding 5g adsorbents mass into 50ml of the prepared stock solution and was shaken with magnetic stirrer at 250rpm and varying contact time (15, 30, 45, 60, 75 & 90 minutes).

Data analysis

The heavy metals concentration of the tannery wastewater samples was analyzed using excel (2013) and SPSS (V. 20). The kinetics of adsorption was analyzed using two kinetic models, pseudo first order and pseudo second order kinetic models and three adsorption isotherms were used to analyze the data obtained.

Results and Discussion

Rice Husk Characteristics

The result of characteristics of rice husk are presented in Table 1

Table 1: Physicochemical characteristics of the adsorbents

Parameters	Rice Husk
Electrical conductivity	0.60 ds/m
Point of zero charge	5.92
Moisture content	0.01
Bulk density	0.386 g/cm^3
Surface area	973-567 (m^2/g)
Surface morphology	Plate 1

Moisture content

Adsorbent Moisture content is a measure of the amount of water present in the adsorbent. It has no effect on the adsorption capacity of an adsorbent, however, high percentage moisture is usually discouraged, this is because high amount of moisture in an adsorbent increases the mass of the adsorbent required during the adsorption process. The moisture content obtained for the rice husk in this study is 0.136% which is better than the 0.7% moisture content reported by Sivakumar (2014). Dada *et al*. (2012) from the study of Sorption of Zn2+ unto Phosphoric Acid Modified Rice Husk and Sivakumar *et al*. (2014) reported much higher percent moisture of 12% and 6% respectively for rice husk silica.

Bulk density

The value of bulk density of prepared sawdust activated carbon as shown in Table 4.2 is 0.386g/cm^3 for rice husk and 0.424g/cm^3 for banana peel and according to Suleiman *et al*. (2012), bulk density for a good adsorbent should not be less than 0.25g/ cm^3. The bulk density of rice husk is better than 0.68 g/cm^3 reported by (Colony and Pradesh, 2012).

Surface morphology

SEM images was obtained to study the surface behavior of rice husk, this image shows a more irregular texture and porous nature of the adsorbent surfaces. This rough irregular surface and increased number of pores indicates higher or increased surface area, (Swarna, 2012). The 4 SEM images labelled a, b, c, and d in Plate I for rice husk with different magnifications of 666x, 477x, 477x and 815x respectively.

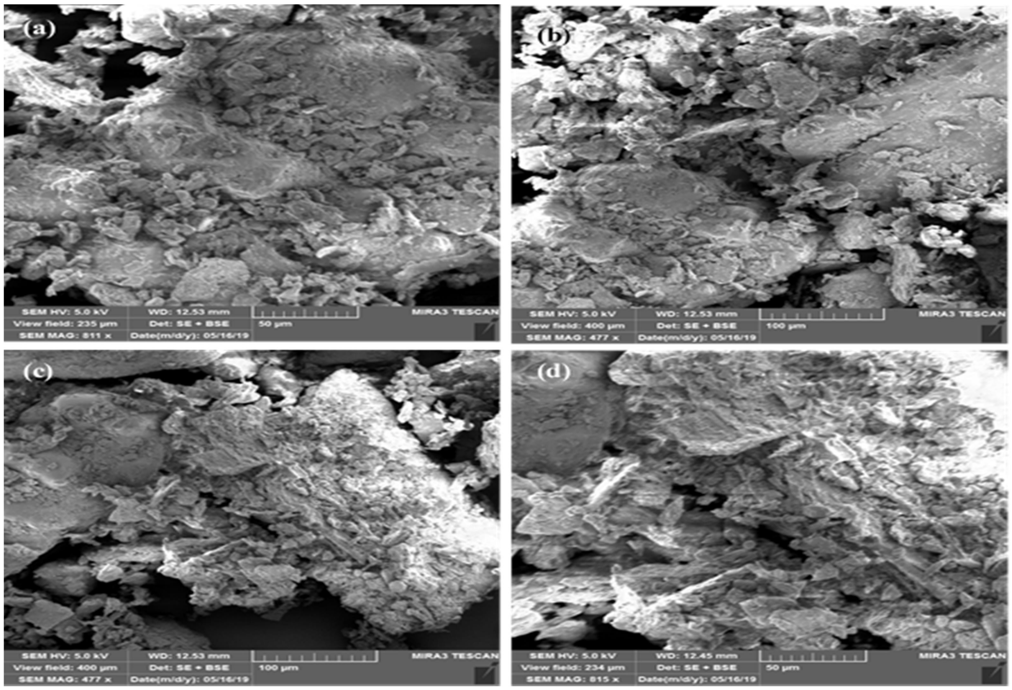

Plate I: SEM images of rice husk

Energy-dispersive-X- ray spectrum (EDS) analysis

The EDS analysis of rice husk, it was observed that $CaCO_3$ and SiO_2 had the highest atomic percentage weight present of 60.05% and 34.19% respectively. While the Au concentration stands for hydrogen concentration. Compounds such as $CaCO_3$ and SiO_2 have been shown to have good adsorption characteristics and high surface area particles (Min *et al.,* 2003).

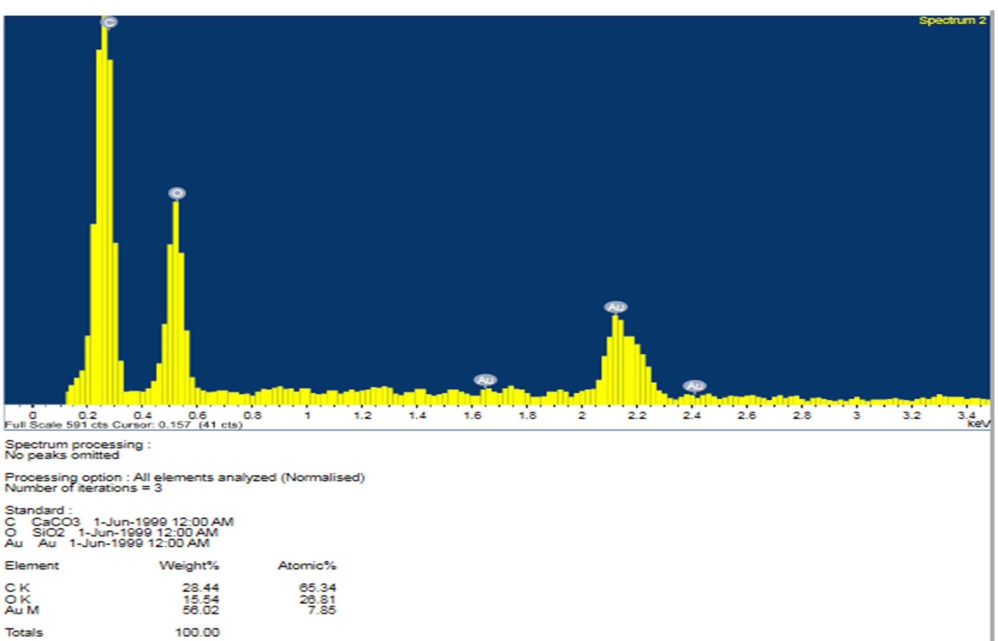

Figure 1: Energy-dispersive-X- ray spectrum (EDS) for rice husk

Dynamic thermos-gravimetric analysis (TGA)

The pyrolysis curve for rate of weight loss and temperature changes. Thermal behavior and temperature dependent decomposition patterns of the adsorbents were investigated by thermo-gravimetric analysis (TGA) under nitrogen environment up to 800^{o}C. Rice husk experienced three modes of weight losses which resulted in total weight reduction by 52% and 64%, respectively. Intercalated and physisorbed water molecules are removed up to a temperature below 200^{o}C in the first stage, and this accounts for 7.5 and 8.5% weight loss. This is followed subsequently by dehy-droxylation (DH), decarboxylation (DC) and removal of other interlayer anions such as nitrates in the second stage of weight loss between 200^{o}C and 300^{o}C, which resulted in 1.2 and 2.5% loss for both. The third stage involves drastic weight loss beyond 300^{o} c with further decarboxylation and dehy-droxylation results in the production of mixed metal oxides. Rice husk experienced two modes of weight reduction which are mainly due to decarboxylation and the interlayer anions removal and formation of MMO. Most of the water molecules have been eliminated due to calcination. Between (35^{o}C and 40^{o} C), the rice husk gained weight due to absorption of water molecules from the environment, and these were subsequently removed with an increase in temperature.

Zeta potential

Zeta potential of each adsorbent in different solutions was averaged with 6 repeats ±1 SD. The rice husk exhibits a negative zeta potential which is a good indication for the adsorption potential of heavy metals.

Point of zero charge

The point of zero charge for Rice Husk sample was determined to be 5.92, The pH at which the positive and negative charges on the biosorbent surface are balanced is often refered to as the point of zero charge (PZC). The pzc differs for different biosorbents (Andersson, 2014). The charged surfaces of mineral particles results in an ability to attract and adsorb dissolved ions. The extent of this ability depends on the specific surface of the particles, as a larger specific surface can contain more charges and thereby attract a larger number of ions (Andersson, 2014).

Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of rice husk indicate complex surface by presence of several peaks with strong absorption band at 3272 cm^{-1} due to O-H stretching from hydroxyl group of caboxylic acid, while the band at 2900 cm^{-1} is due to C-H absorbance typical of organic material. The band 1603 cm^{-1} indicates the presence of cabonyl group via strong absorbtion, which further coroborates the band at 3272 cm^{-1} by an up field shift while the band at 1319 cm^{-1} coroborates the band at 2900 cm^{-1} in establishing the presence of C-H group through bending absorption. The band at 1033 cm^{-1} reveals the presence of an ether type C-O-R bond via stretching absorption as shown in Figure 2.

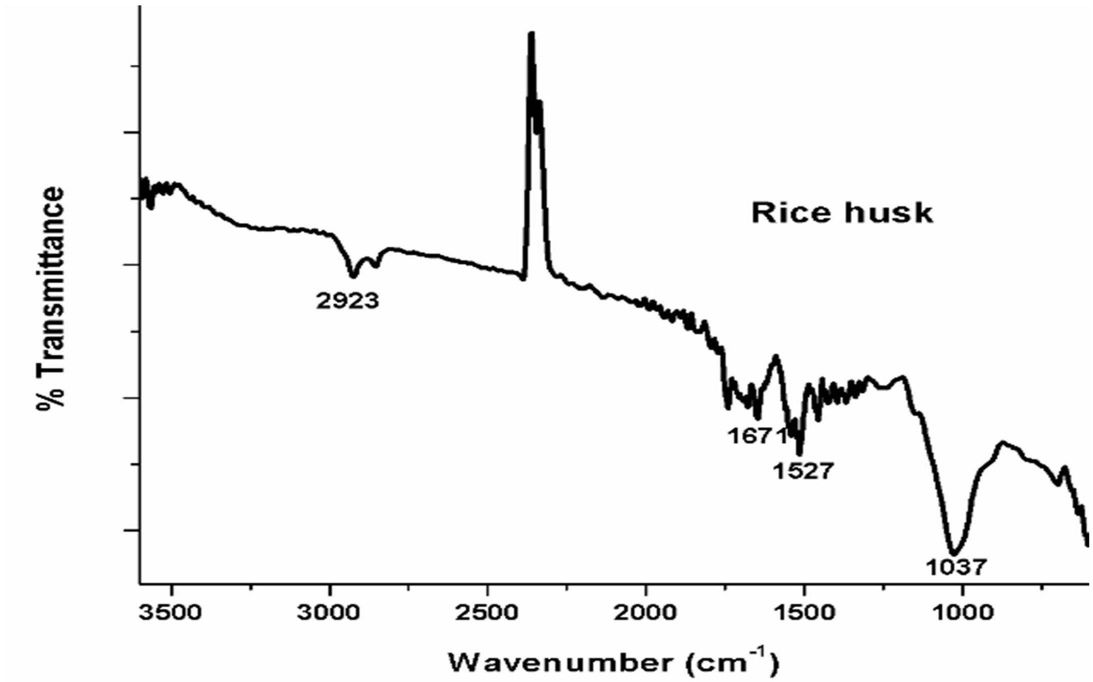

Figure 2: FTIR curve for rice husk

Batch Adsorption Tests

The batch adsorption was carried out with varying adsorbent dosage and contact time at ambient room temperature. The effect of adsorbent dosage was studied at 5g/l, 10g/l, 15g/l, while the effect of contact time was observed at 60min, 120min, and 180min. Figure 3 shows the variation of percentage removal of Chromium with time and rice husk dosage.

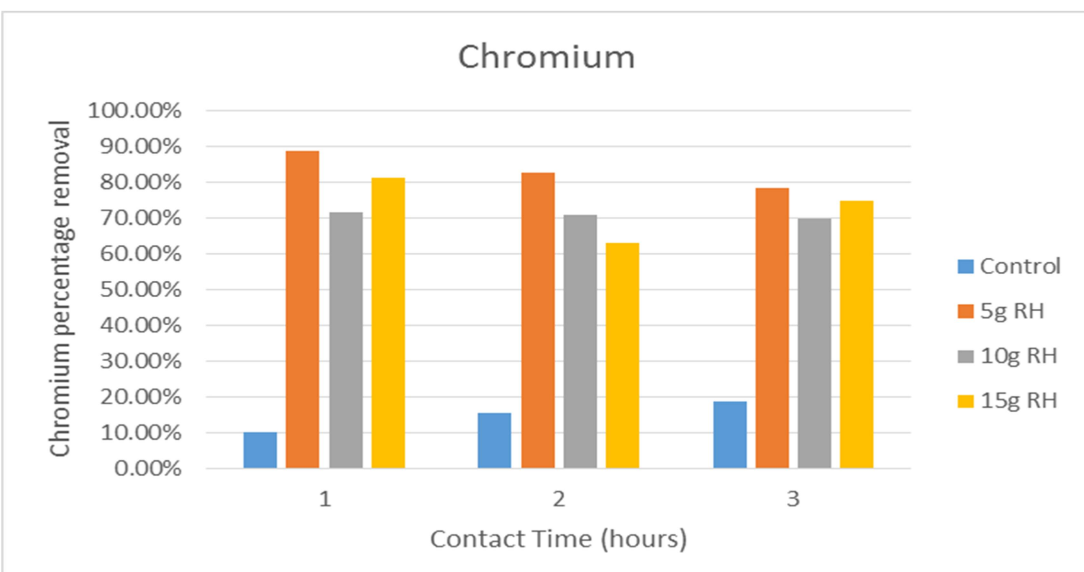

Figure 3: Effect of time and RH dosage on percentage removal of Chromium

The adsorption of Chromium did not show consistent increase in adsorption process with increased adsorbent dosage. The percentage removal of Chromium can be observed to be optimum with 5g rice husk dosage for the 1hr agitation time (88.6%), 82% for the 2hr and 78% for the 3hr respectively. Hence 1 hour can be considered optimal percentage removal time for chromium using 5g RH. On the other hand, 10g RH shows no significant increase or decrease in Chromium percentage removal with agitation time variation, 72% for the 1 hour to 73% for the 2 hour and 71% for the 3 hour respectively. Hence 2 hr can be considered optimal percentage removal time for 10g RH. Similarly, for 15g RH there is a drastic decrease in Chromium percentage removal for the 1 hour and 2 hour (83% and 63%) respectively, then increase in percentage removal (75%) for the 3 hour shaking time. Hence, the optimal percentage removal time for 15g RH is 1 hour. The reference sample (control or 0 g RH) shows slight percentage removal of Cr 10% for 1 hour agitation time, 16% for 2 hour and 19% for 3 hours respectively probably due to adsorption by the container walls.

About 90 % removal of Cr(VI) in an aqueous solution using rice husk ash was achieved by Anand *et al.*, (2014). Whereas, Singh and Singh, (2012) found that the maximum removal (94 %) of Cr (VI) using rice husk carbon. Nearly 79.94 % removal of Cr(VI) in a tannery industry wastewater was only achieved using rice husk (Swathi *et al*., 2014) and the removal percentage of 88.3 % in a tannery industry using rice husk silica powder (Sivakumar, 2015). This study removed the maximum of Cr(VI) in a tannery industry wastewater with 88.6%. The maximum removal of Cr(VI) in an aqueous solution achieved with the contact time of 180 min. (Singha *et al*., 2011), 100 min. (Anand, *et al*., 2014) and 60 min (Sivakumar, 2015). This study removed the maximum of Cr(VI) in a tannery industry wastewater rather than the aqueous solution with the contact time of 60 min. Figure 4 shows the variation in percentage removal of cupper with time and rice husk dosage.

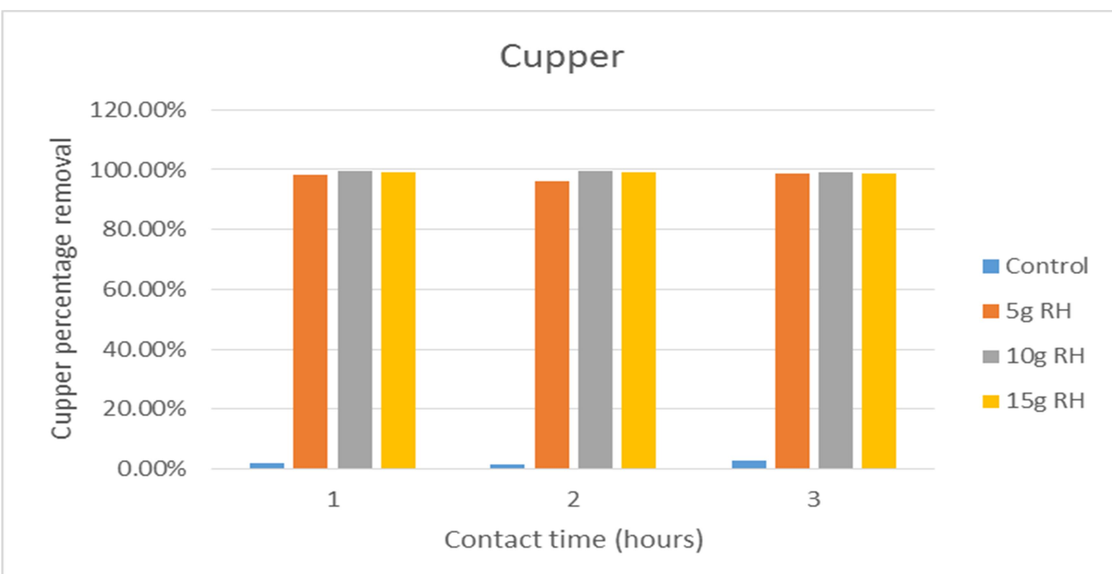

Figure 4: Effect of time and RH dosage on removal of Copper.

The percentage removal can be seen to be (98%, 96%, 98.9%) 5g RH, (99.6%, 99.7%, 99.1%) 10g RH, (99.1%, 99.3%, 98.7%) 15g RH for 1, 2 and 3 hour agitation time respectively. A slight percentage removal was observed in the control sample of 1.99%, 1.44%, and 2.92% for 1, 2 and 3 hour contact time. Figure 5 shows the variation in percentage removal of cadmium with time and rice husk dosage.

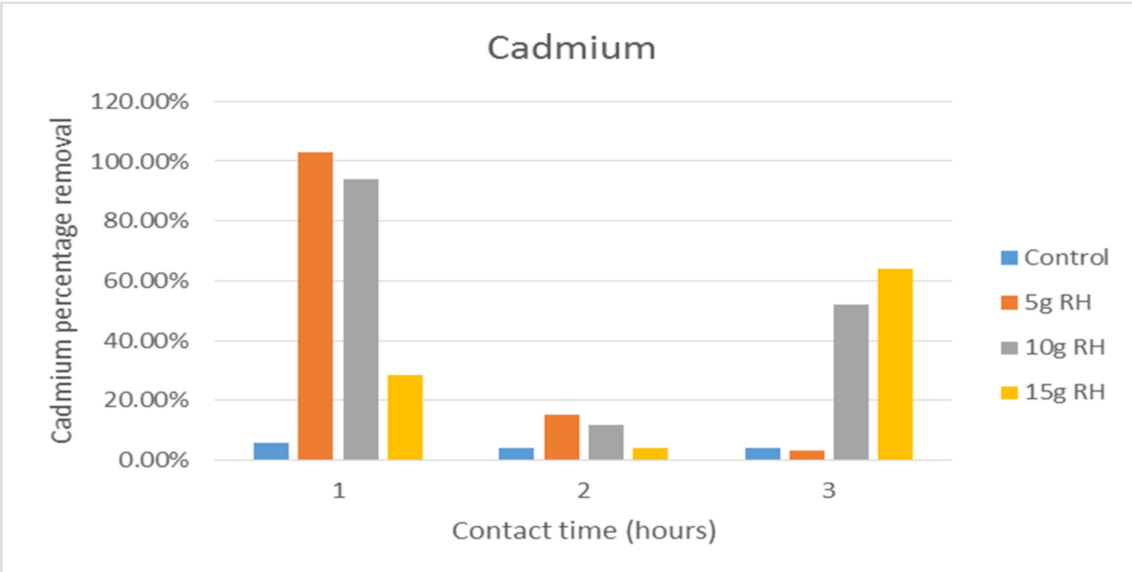

Figure 5: Effect of time and RH dosage on removal of Cadmium

The percentage removal can be seen to be (102%, 14.9%, 3%) 5g RH, (93.9%, 11.6%, 98.89%) 10g RH, (28.6%, 3.9%, 64%) 15g RH for 1, 2 and 3 hour agitation time respectively. There is also a slight percentage removal of (5.7%, 4.2%, 4%) in the control sample for 1, 2, and 3 hour agitation time. Figure 6 shows consistent increase in percentage removal of BOD, COD, PO_4 and NO_3 with increased adsorbent dosage.

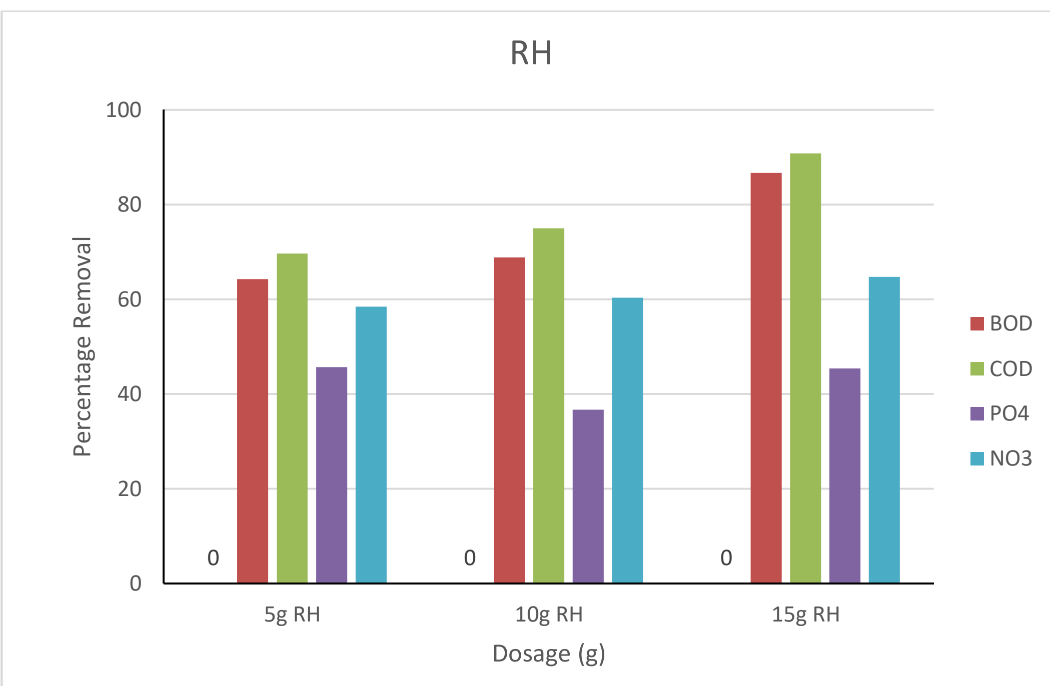

Figure 6 Effect of rice husk dosage on BOD, COD, PO_4 and NO_3

The percentage removal of BOD, COD, PO_4 and NO_3 can be observed to be (64.29%, 69.69%, 45.71%, 58.48%) for 5g RH dosage, (68.89%, 75%, 36.71%, 60.34%) for 10g RH dosage and (86.67%, 90.82%, 45.41%, 64.71%) for 15g RH respectively.

Adsorption isotherms

Two isotherm equations were adopted in this study, the Freundlich and Langmuir equations.

Freundlich isotherm equation

The plot of the linerarised form of the Freundlich isotherm equation is shown in Figure 7, which is a plot of ln qe against ln ce. The Freundlich isotherm constants K_f and n, and the correlation coefficient are listed in Table 4.6.

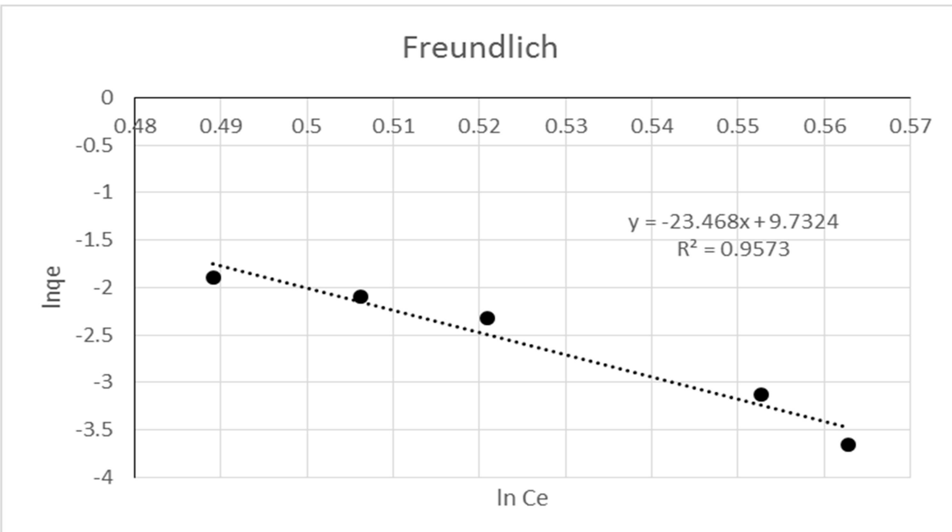

Figure 7: Freundlich isotherm model for sorption of chromium

Table 2: Adsorption Isotherm Parameters

Isotherm Model	PARAMETERS	Rice Husk
Freundlich	K_f (min^{-1})	1684
	1/n	0.0426
	R^2	0.9573
Langmuir	K_L (l/mg)	1.623
	Q_{max}	0.00236
	R^2	0.8532
	R_L	0.2636

Boparai et al. investigate the adsorption of lead (II) ions from aqueous solutions using coir dust and its modified extract resins. Although several isotherm models were applied, the equilibrium data was best represented by Freundlich and Flory-Huggins isotherms due to high correlation coefficients (Ayawei *et al*., 2017).

Langmuir isotherm equation

The plots of Ce/ Qe against Ce for the Langmuir equation are shown in Figure 7 indicating the adsorption of chromium on rice husk powder give a straight line.

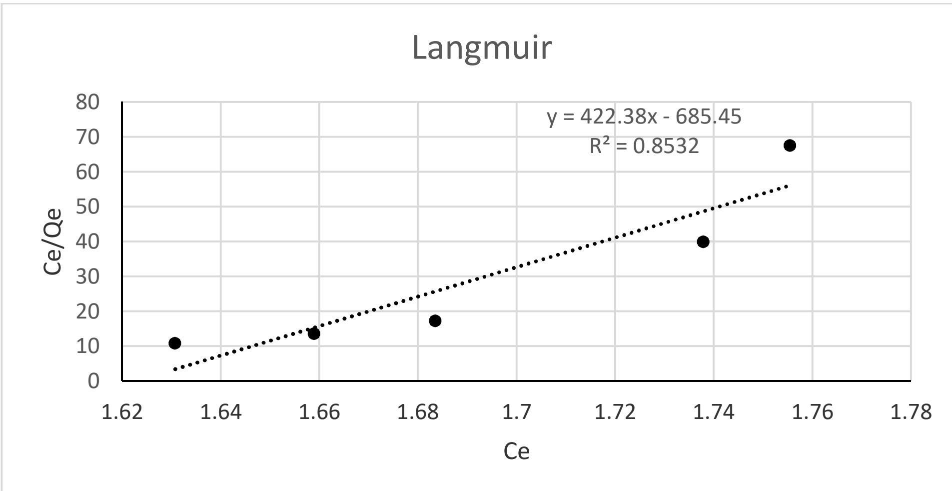

Figure 8: Langmuir isotherm model for sorption of chromium

The Langmuir Separation factor, R_L is a dimensionless constant and is essential characteristic of Langmuir isotherm model. The Langmuir isotherm constant and the correlation coefficient R2 are listed in Table 4.6. The small value of R_L (0.2636) indicates a favorable adsorption.

Adsorption Kinetics Studies

The plot of linearized form of the pseudo-first order equation is shown in Figure 8, which is a plot of log (q_o-q_t) against time (minutes).

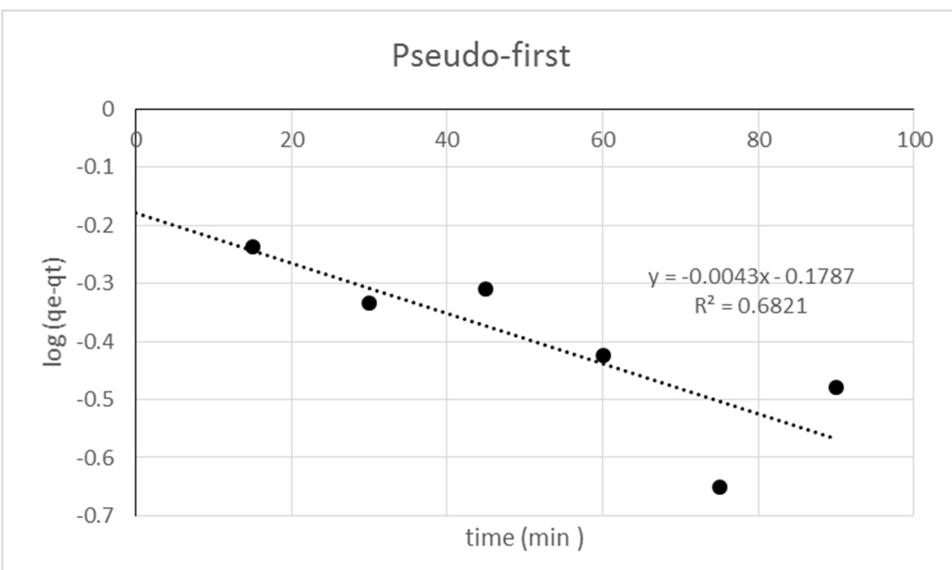

Figure 9: Pseudo-first order sorption kinetics of Cr^{6+}

The pseudo first-order rate constant k_1, amount of Chromium ion adsorbed at equilibrium q_e, and correlation coefficients are shown in Table 4.7 as 0.0099, 0.015mg/g and 0.6821. The plot of linearized form of the pseudo-second order equation is shown in Figure 9.

Table 3: Adsorption Kinetic Parameters

Kinetic Model	PARAMETERS	RICE HUSK
Pseudo 1st	k_1 (min^{-1})	0.0099
	q_e (mg/g)	0.015
	R^2	0.6821
Pseudo 2nd	k_2 ($gmg^{-1}min^{-1}$)	0.1009
	q_e(mg/g)	95.23
	R^2	0.9878

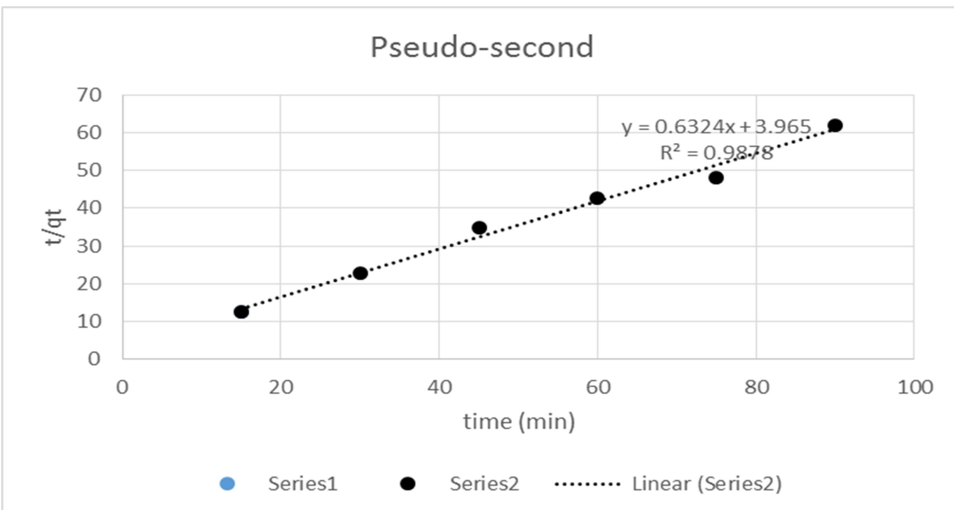

Figure 10: Pseudo-second order sorption kinetics of Cr^{6+}

The results showed that, the correlation coefficients, R^2 obtained for pseudo first order kinetics model was 0.6821 which is very low compared to the pseudo second order kinetics model constants. The pseudo-second order plot showed a R^2 value of 0.9878, experimental q_e value of 0.0158mg/g and the pseudo-second order rate constant $k_2$value of 0.1009 as shown in Figure 4.23, which is a plot of t/q against t. Therefore, the data fitted better with pseudo second-order kinetic model based on the correlation coefficient.

ANOVA for Cadmium, Chromium and Copper Percentage Removal by Dosage

Table 3 shows the Analysis of Variance for Cadmium, Chromium and Copper percentage removal by dosage with a significant value of p = 0.002, 0.000, 0.000 respectively. This implies that there is change or significant difference in Cadmium, Chromium and Copper removal between the different levels of dosage with reference to the control sample.

Table 4: ANOVA for Heavy Metals Percentage Removal by Dosage

		Sum of Squares	df	Mean Square	F	Sig.
Cadmium	Between Groups	2.329	10	.233	3.089	.002
	Within Groups	7.993	106	.075		
	Total	10.323	116			
Chromium	Between Groups	7.525	10	.752	107.122	.000
	Within Groups	.745	106	.007		
	Total	8.269	116			
Copper	Between Groups	8.059	10	.806	4724.741	.000
	Within Groups	.018	106	.000		
	Total	8.077	116			

Conclusion

The study revealed that the tannery effluent contains pollutants that are beyond the NESREA discharge limit, hence, should be treated prior to disposal. The results obtained from the characterization of the adsorbents indicated that the prepared bio-sorbents have good adsorptive properties. The use of rice husk mixture in the treatment of tannery effluent, indicated good adsorbent still, rice husk is more effective in removing chromium from tannery effluent. The rice husk is an effective adsorbent in the treatment of tannery effluent prior to disposal with a COD, BOD, Nitrate and phosphate removal. Optimum operating conditions are concluded to be a contact time of 60 minutes at an adsorbent dosage of 5g at ambient room temperature. Experimental data has well fitted into Freundlich isotherm model and second-order kinetic model suggesting second-order nature of the process, clearly indicating that one metal ion is absorbed onto two sorption sites on the adsorbent surface.

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