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Comparative adsorption studies of Cr(VI), Pb(II) and Cd(II) ions onto Tiger-nut activated carbon-zeolite composite

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Abstract

The need to develop a new effective and efficient adsorbent for pollutant removal is insatiable. Tiger-nut activated carbon-zeolite composite (STC) was prepared using sol-gel method by mixing zeolite A and prepared steam activated carbon from tigernut using thermal method for removal of Cr (VI), Pb (II) and Cd (II) from aqueous solution. The material was characterized by Fourier transform infrared (FTIR), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX) and Brunauer–Emmette–Teller (BET) respectively. Characteristic vibrational frequency surface area methods. The surface areas and average sizes of the spherically rode-like embedded nanomaterial were 62.20 m^2/g and 41.11 nm. The effect of initial concentration, adsorbent dosage, contact time, pH and temperature on the adsorption capacity were experimentally determined. In adsorption isotherm and kinetics: Langmuir, Freundlich, Temkin, Pseudo-first order, Pseudo-second order and thermodynamic were applied to estimate the adsorption capacity of the adsorbent. From the results obtained, tigernut-zeolite composite showed maximum adsorption of 129.870, 263.158 and 126.582 mg/g for Chromium, Lead and Cadmium respectively.

Keywords: *Adsorbtion; Kinetics; Isotherms; Thermodynamics.*

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1. INTRODUCTION

Pollution due to heavy metal uses have been greatly increased, because of their vital presence in many important industries, such as batteries, mining, tanning, pigments, fertilizer and others. Thus, large quantities of waste water contaminated with heavy metals have been discharged directly to the aquatic environment without an adequate treatment which causes environmental problem worldwide (Alalwan *et al.,* 2020). Therefore, hazardous heavy metals removal from the effluents polluted with the heavy metals has become a great challenge in the field of environmental sciences (Alkali *et al.,* 2022a). The presence of those metals such as Cr, Pb, Cd Cu, Zn, Ni, Mn and Hg, etc in the aquatic life is a special issue because they are non-degradable, persistent, toxic and may lead to various harsh diseases (Abdus-Salam *et al*., 2023).

Chromium, lead and Cadmium have different applications in many industries. However, high concentrations of chromium, lead and cadmium are carcinogenic and highly toxic metals which can lead to numerous diseases and disorders such as, destruction of testicular tissue and red blood cells, kidney damage, anaemia, reproductive system damage, nervous disorders, low yield production in plant and sickness even death (Ayob *et al.,* 2021; Ya *et al.,* 2021). Discharging these metals to water body would be dangerous to the humans, plants and aquatic animals in the environment and causes many harmful effects when their concentrations exceeded the acceptable limit (Adekola and Abdus-Salam, 2018; Abdellaoui *et al.,* 2019).

Years ago, numerous methods have been employed to remove these heavy metals from wastewater such as, chemical precipitation, (Zhou *et al.,* 2017) membrane filtration, (Chowdhury *et al.,* 2019) ion-exchange (Kołodyn´ska *et al.,* 2017) and reverse osmosis (Huang *et al.,* 2016). However, adsorption method is considered to be the best method due its simplicity, environmentally friendly and required less technology (Oyewumi-Musa *et al.,* 2023). Therefore, zeolites as an adsorbent have been used for the characterization and adsorption studies due to its outstanding properties in material science.

Zeolites belong to the class of crystalline aluminosilicates and were discovered as natural mineral. The composition of the zeolite group of substances can be described by formula

$Me_{2}/nO{\cdot}Al_{2}O_{3}{\cdot}xSiO_{2}{\cdot}yH_{2}O$,

where the factor n indirectly determines the charge of the cation Me, which is typically present as an alkali or alkaline earth cation (Koshlak, 2023). The factor y indicates the number of molecules contained in the crystal. Zeolites are microporous crystalline aluminosilicates with three dimensional frame work structures containing SiO_4 and AlO_4^- tetrahedrons, linked together with adjacent tetrahedrons that share oxygen to form distinctive crystalline structures, containing large vacant cages that can accommodate cations (Belviso, 2018). The molar ratio of SiO_2 to Al_2O_3 in the empirical formula is called module (x).

Zeolites are inorganic crystalline micro porous minerals (pore diameter < 2 nm) having widespread application such as heterogeneous catalysis, ion-exchange, adsorption and separation process in the petrochemical, electrochemistry, refinery food industries, pharmaceutical and medical engineering (Jiang *et al.,* 2018; Ahamdi *et al.,* 2022). Zeolites have been used as purely or composites with other adsorbent because of their properties of abundance of easy-exchange cations present in three-dimension porous structure, acidity, unique topology, high structure stability, large surface area, and uniform pore size (Aljerf *et al.,* 2018; Zhang *et al.,* 2023).

In the present study, the optimum conditions which affects the removal of Cr (VI), Pb (II) and Cd (II) ions were investigated. Similarly, some isotherm, kinetic and thermodynamic models were applied to the experimental data to understand the chemistry between the adsorbent and the adsorbates. Moreover, this work revealed a modified method for preparing a composite of synthezed zeolite and active carbon prepared from tiger-nut chaff which is a cheap natural waste.

2. MATERIALS AND METHOD

Preparation of Modified Zeolite

A 50 g of the raw kaolin was soaked with 125 mL of distilled water. The mixture was allowed to age for 72 hours with constant stirring. In this process of sedimentation, the water on the top was decanted and replaced with fresh one. On the third day, the lower density suspension which mainly composed of kaolinite was decanted to another container and the denser one which is predominantly quartz was discarded. The suspended mixture was separated using 63 micro meter mesh and dried (Verrecchia *et al.,* 2022).

The dried material was subjected to ultrasonic suspension by mixing it with water in the ratio (4 g: 400 mL) at a temperature of 40 ^{o}C for 30 minutes followed by the removal of non-structural iron by magnetic separation at different time intervals of magnetic stirring (Aldahri, 2019). The suspension with lower density was decanted, filtered and dried in an oven at 80 ^{o}C. The dried product was pounded and further sieved using 200 micro meter mesh size (Alkali *et al.,* 2025).

In this method of zeolite A synthesis, alkali fusion (solid-state reaction) step was introduced before the calcination step to extract aluminium and silicon from the starting raw kaolin. This method has the advantage of the kaolin and other impurities like quartz being expected to be completely activated and converted to zeolite A due to alkali and thermal activation (Jha and Singh, 2016). Thus, 10 g of the raw kaolin was dry-mixed with 12 g of NaOH (solid) for 30 min followed by calcination at 600 °C for 1 hr in a crucible put in a muffle furnace. Then the fused product was ground in a mortar and mixed with 100 mL of the ultra-pure distilled water and stirred (500 rpm) at 50 °C for 1 hr for gel formation (Basaldella *et al.*, 2009). Finally, the product obtained was filtered, washed and oven dried over night at 80 °C and stored in a plastic container for characterization (Lijalem, 2016).

Zeolite-tigernut chaff composite preparation

Equal mass ratio (50 g) of steam activated tiger nut and synthetized zeolite were mixed together and subjected to heat in muffle furnace at 600 °C for 1 hour then removed and cooled in desiccator after one hour. The solidified product was then ground using pestle and mortar. A 250 mL of deionised water was added, stirred for one hour using magnetic stirrer at 50 °C then washed to neutral pH, dried for 60 °C for 9 hours in air and stored for characterisation and adsorption processes (Sivalingam and Sen, 2018).

Preparation of the Adsorbates

Stock solutions of Cr, Pb and Cd at concentrations ranging from 200-1200 mg/L were prepared using deionized water. The desirable concentrations were prepared through the adequate dilution of stock solution with deionized water. The primary pH was adjusted using NaOH or HCl. Initial metal concentrations were measured using a UV-visible spectrophotometer for chromium and a flame atomic adsorption spectroscopy for Pb and Cd respectively.

Calculations ofCr(VI), Pb(II) and Cd(II) uptakes

A 20 mL of Cr(VI), Pb(II) and Cd(II) solution with initial concentrations ranging between 200 and 1000 mg/L were added onto 0.01 g of samples in 100 mL Erlenmeyer flask. The sample were agitated on orbital shaker for 5 h at 230 rpm. The supernatant liquids were filtered, the residual metal analysis were carried out using Buck Scientific Model 210 VGP Atomic Absorption Spectrophotometer (AAS), and the quantity adsorbed were calculated from Eq. 1 (Alkali *et al.*, 2022a):

$$Q = \frac{(C_o - C_e)}{W} \times V \tag{1}$$

and the extent of adsorption was calculated from Eq. 1 (Alkali *et al.*, 2022b):

$$\%\,R = \frac{(C_o - C_e)}{C_o} \times 100 \tag{2}$$

Where *qe* is the quantity of metal adsorbed (mg/L); *Co* and *Ce* are the initial and final concentrations of the metals (mg/L), *V* is the volume of the metal solution (L), and *M* is the mass of the adsorbents (g) used. The quantity adsorbed were plotted against the initial concentration to determine the adsorption capacity of the STC sample for Cr(VI), Pb(II) and Cd(II) ions. These optimal concentrations were used subsequently for determination of other dependable factors of adsorption studies.

3. RESULT AND DISCUSSION

Characterisation of zeolite-prepared Tigernut chaff composite

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR analysis was carried out in order to identify the different functional groups present which could be responsible for the adsorption process. Some of the peaks appearing in the FT-IR spectrum were assigned to various functional groups according to their respective wavenumbers. Figure 1 below shows the spectra of the adsorbent.

The broad and intense peak around 3427.95 cm^{-1} was attributed to the stretching of O-H group due to inter and intramolecular hydrogen bonding of polymeric compounds such as alcohol or phenols as in cellulose, lignin and hemicellulose (Renu *et al.*, 2017). The peak observed at 2360.95 cm^{-1} was associated with stretching vibrations of CO_2. The peak at 1377.22 cm^{-1} was assigned to be C-H bond of aldehyde groups. The peak around 1620.26 cm^{-1} corresponds to the C=C stretching which might be attributed to the presence of lignin aromatic bond (Adegoke *et al.*, 2020). The intense peak of 1024.24 cm^{-1} corresponds to the C-O stretching of alcohol or carbonxylic acid (Musa and Alkali, 2023). The peak at 1230.63 which cm^{-1} was a plane vibration absorption peak of hydroxyl from cellulose.

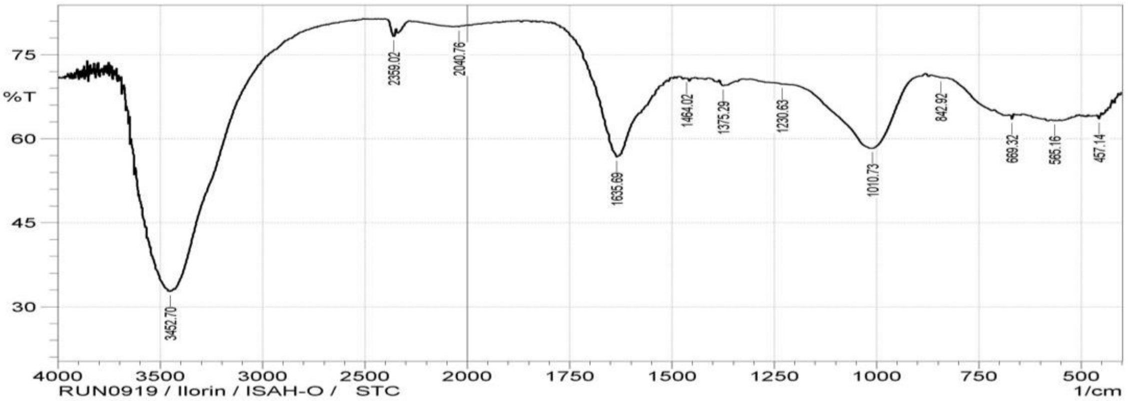

Figure 1: *FT-IR Spectrum for STC*

Scanning Electron Microscopy (SEM)/Energy Dispersive X-ray (EDX) analysis

The SEM micrographs enable the direct observation of the surface microstructure of STC. Figure 2a & b illustrates the SEM micrographs of STC at 10 μm and the EDX results respectively. Similarly, EDX analysis of STC was carried out to identify the elemental composition of the aforementioned adsorbents. The SEM micrograph of STC shows irregular and porous structure which suggested that it may act as better adsorbent.

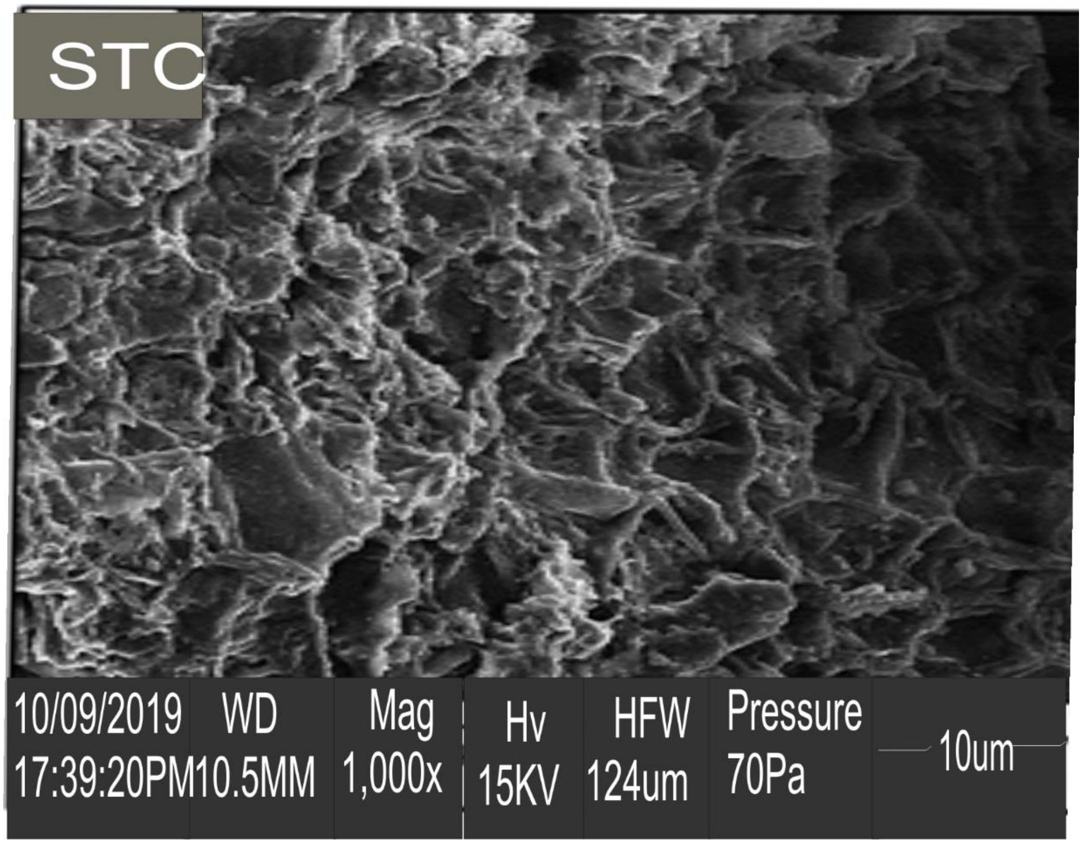

Figure 2a: *SEM micrograph of STC*

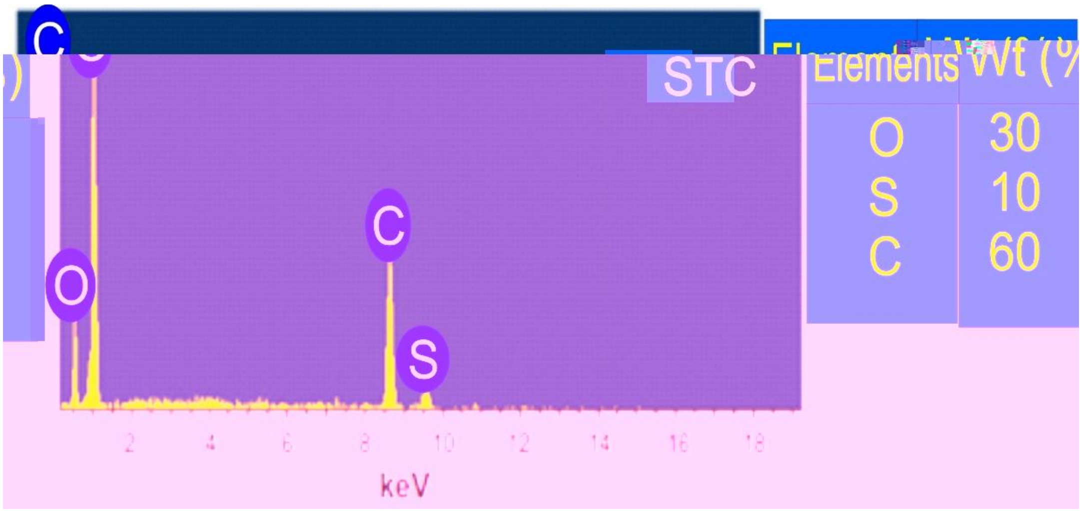

Figure 2b: *EDX analysis showing the elemental composition of STC*

Brunauer-Emmett-Teller (BET)

BET theory aims to explain the physical adsorption of gas molecule on a solid surface and serves as the basis for an important analysis technique for the measurement of specific surface area, pore size distribution, pore diameter and pore volume (Alkali and Fatimah, 2023). It is known that the higher the surface area and the pore volume, the smaller the pore diameter and pore size distribution of the adsorbent, and the better the adsorption capacity (Brunauer *et al.*, 1938). From Table 1, the highest pore volume for STC is 55.8 cc/g at 7.90 ($p/po \times 10^{-2}$). The better pore size distribution of this adsorbent is 0.70 at 350 um sieve mesh (micron) and the specific surface area of these studied adsorbents was 1300 m^2/g at 300 ^oC.

Table 1: *BET analysis for STC*

Temp (^{o}C)	**Surface area (m^2/g)**	**Sieve Mesh (micron)**	**Pore Size Distribution**	**Relative Pressure (P/P_0 X 10^{-2})**	**Volume (cc/g)**
100	1022.42	<20um	2.05	3.50	10.8
200	1021.41	20-40um	12.85	4.50	16.6
300	1300.21	40-100um	54.00	6.50	24.5
400	992.50	100-350um	30.35	6.90	34.2
500	1011.20	350um	0.74	7.50	45.4
600	1022.60	Total	99.99	7.90	55.8

Adsorption studies

Effect of initial concentration

The effect of initial concentration of the chromium, lead and cadmium on the uptake by tiger-nut-composite (STC) was shown on Figure 3, using 0.05 g of STC for Cr (VI), Pb (II) and Cd (II) ions respectively. The maximum adsorption capacities are 69.26 mg/g at 1100 ppm, 215.99 mg/g at 1000 ppm and 207.68 mg/g at 900 ppm for Cr (VI), Pb (II) and Cd (II) ions respectively. It is observed that adsorption of Cr (VI), Pb (II) and Cd (II) ions increased with increase in metal ion concentration. This due to the fact that there is less competition between the low adsorbate concentration and the binding site of the adsorbent, while at higher concentration, there is a corresponding increase in the driving force, thereby enhancing the interaction between the metal ions in the aqueous phase and the active sites of the adsorbents (Alkali *et al.*, 2023). Similar results were obtained on the adsorption studies of zinc (II) on magnetite, baobab (*Adansonia digitata*) and magnetite–baobab composite reported by (Abdus-Salam and Adekola, 2018).

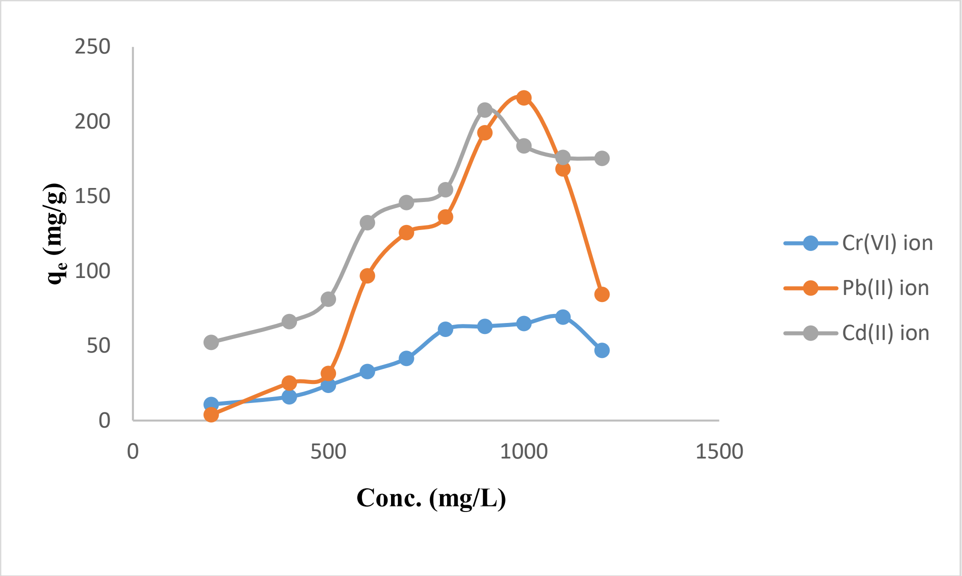

Figure 3: *Effect of Initial Conc. of Cr (VI), Pb (II) and Cd (II) ions onto STC*

Effect of adsorbent dose

The influence of using varying amounts of adsorbents (0.01–0.05 g) while adsorbate initial concentrations were fixed as shown in (Figure 4) that is the adsorbent dosage was increased, the amount adsorbed also increased but the amount adsorbed per unit mass of the adsorbent decreased considerably for all the metal ions. The results show that the maximum adsorption for Chromium, Lead and Cadmium are 564.2857 mg/g, 461.9475 mg/g and 259.1713 mg/g respectively. When the agitation speed and reactor size are kept constant after optimization of these parameters, increasing the adsorbent dose will reduce accessibility of adsorbate to the active sites on the adsorbent. The decrease in adsorption per unit mass with increasing dose of adsorbent is attributed to possible overlapping of adsorption sites as adsorbent dose increases or clogging of adsorbent which will equally reduce the effective adsorption sites (Amare, 2019).

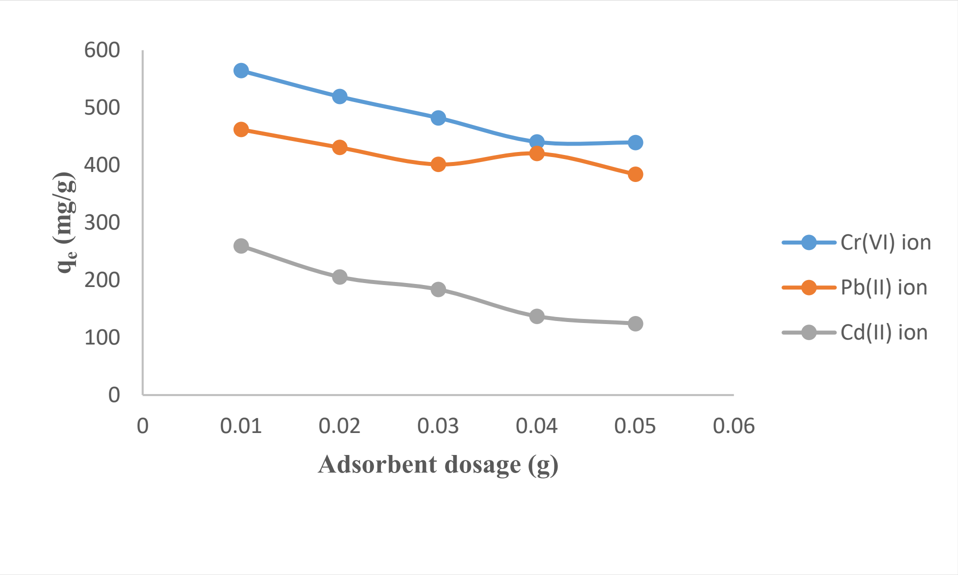

Figure 4: *Effect of adsorbent of Cr (VI), Pb (II) and Cd (II) ions sorption onto STC*

Effect of contact time

Time has a greater influence on the adsorption process as it provides insight into the rate of reaction and the time the adsorption process reaches equilibrium (Abdus-Salam *et al.*, 2023). The effect of time on adsorption effectiveness is shown in Figure 5. Experiment was conducted by varying contact time from 30, 60, 90, 120, 150 and 180 minutes for chromium, lead and cadmium while maintaining all other optimal conditions constant as attained in the earlier experiments. The maximum quantity adsorbed for Cr (VI), Pb (II) and Cd (II) ions onto STC are 670, 1083.82 and 845.16 mg/g for chromium, lead and cadmium at 150, 120 and 150 minutes respectively. This means that the reaction between the adsorbents and the adsorbate could be obtained at this time aforementioned above and it is used for subsequent experiment. The increase in percentage removal with increase in contact time can be explained owing to a larger surface area of the STC available at the beginning of adsorption of heavy metals ions. Again, as the contact time increased which also increased Cr (VI), Pb (II) and Cd (II) ions adsorption and it remained practically constant after the equilibrium was reached. As the binding sites became used up, the adsorption rate slowed down due to competition of adsorbate for the little remaining or available active sites in the adsorbent (Saidur, 2013)

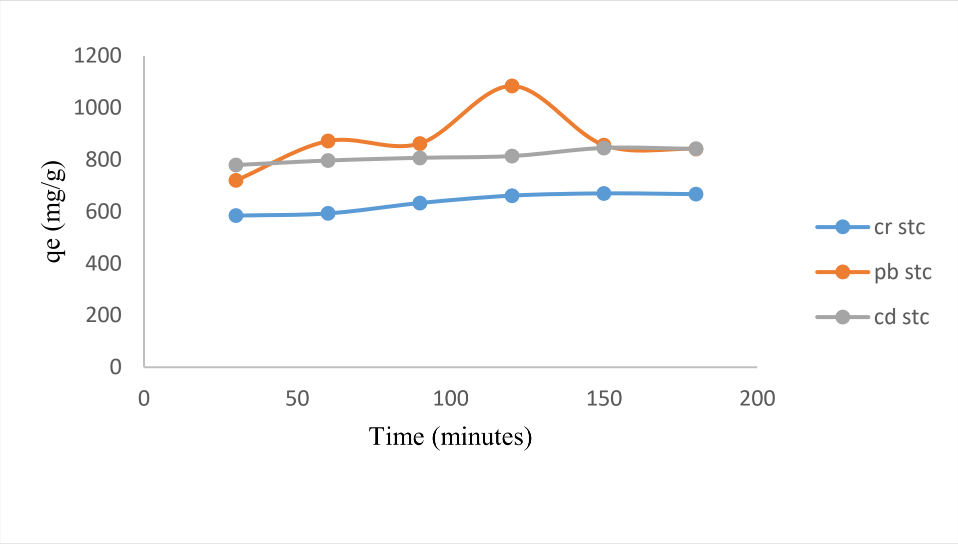

Figure 5: *Effect of contact Time on Cr (VI), Pb (II) and Cd (II) ions onto STC*

Effect of pH

The pH of solution significantly affects the adsorption process of heavy metals from aqueous solution hence it is an important condition that controls the adsorption processes of Cr (VI), Pb (II) and Cadmium (II) onto STC. Batch adsorption studies at different pH were carried out in the range of 2, 3, 4, 5, 6, 7 and 8. The data obtained were clearly shown in Figure 6, while maintaining all other optimal experimental conditions constant as earlier attained for all the metal ions. It is shown that the quantity adsorbed increased with increase in pH. At low pH, high concentrations of H^+ ion were present in solution that compete for empty adsorption sites of the adsorbent. This account for the observation of fast increase in percentage removal as the pH increased. For every hydrolysable metal ion, there was a critical pH values where the adsorption of metal ion efficiency increases from a very low level to maximum value (Alkali *et al.*, 2022b).

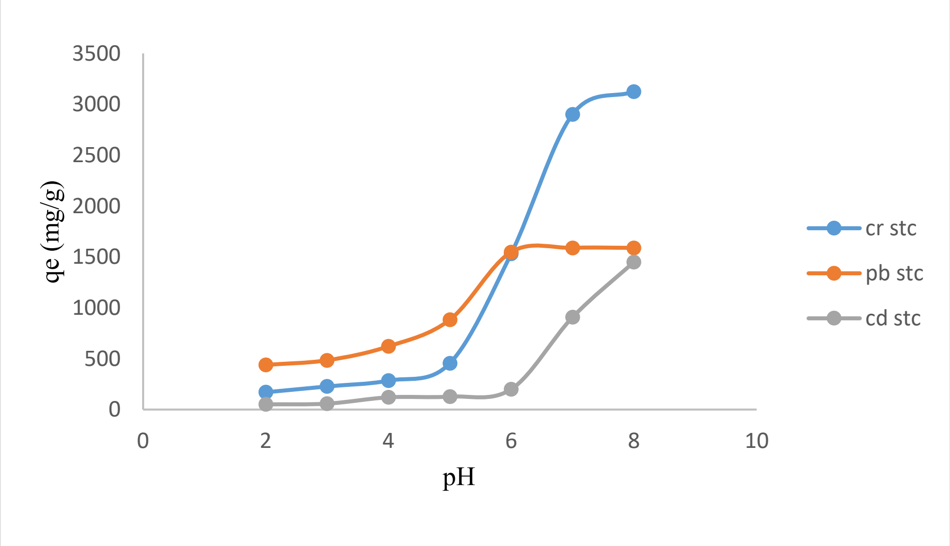

Figure 6: *Effect of pH on Cr (VI), Pb (II) and Cd (II) sorption onto STC*

Effect of temperature

The effect of temperature on chromium, lead and cadmium on the surface of STC in different temperature range (30, 40, 50, 60, 70, 80 and 90 °C) were investigated and the results obtained are shown in Figure 7. It was generally observed that the quantity and percentage adsorbed was increased with increase in temperature. The maximum quantity adsorbed of Cr (VI), Pb (II) and Cd (II) ions onto STC are 681.43, 1589.33 and 1446.04 mg/g respectively at 90 °C. The steady increase in the removal efficiency of the adsorbent for the metal ions is probably due to the effect of temperature on the interaction between the adsorbent surface and the metal ions in the aqueous solution. The above results showed that the adsorption was endothermic in nature (Abdus-Salam and Bello, 2015)

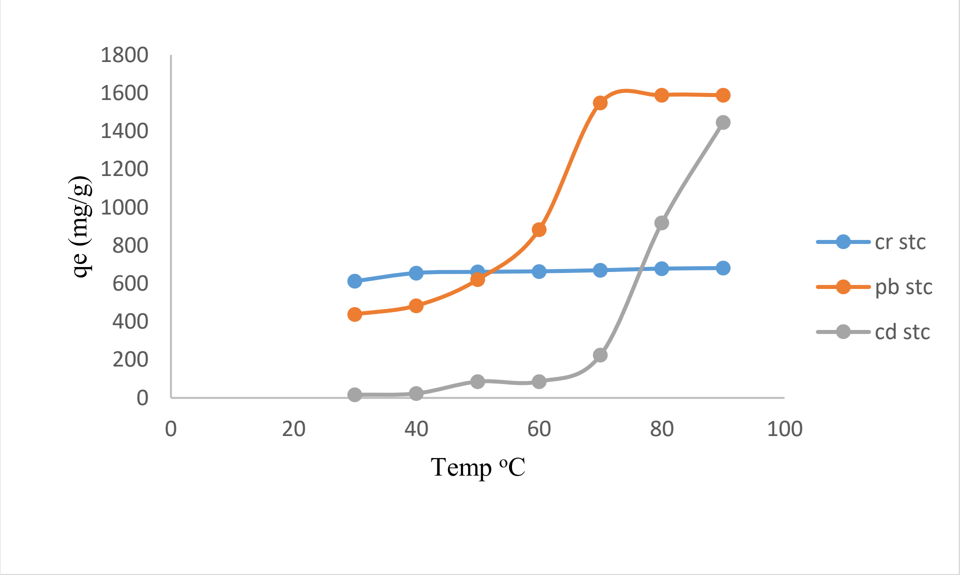

Figure 7: *Effect of Temperature on Cr (VI), Pb (II) and Cd (II) sorption onto STC*

4. CONCLUSION

This study investigated the comparative adsorption studies of Cr(VI), Pb(II) and Cd(II) ions onto tiger-nut activated carbon-zeolite composite. Tiger-nut activated carbon-zeolite composite (STC) was prepared with sol-gel method by mixing zeolite A and prepared steam activated carbon from tigernut using thermal method for removal of Cr (VI), Pb (II) and Cd (II) from aqueous solution. The mixture was allowed to age for 72 hours with constant stirring. The steam activated tiger nut and synthetized zeolite were mixed together and subjected to heat in muffle furnace at 600 °C for 1 hr and the results were subjected to characterization and adsorption studies. The results of FTIR spectrum revealed broad and intense peak around 3427.95 cm^{-1} which was attributed to the stretching vibration of O-H group due to inter and intramolecular hydrogen bonding of polymeric compounds. The adsorption results obtained indicated the adsorbent is very fast and efficient in removal of chromium, lead and cadmium respectively. The achievement of this result also justifies the significance or effectiveness of the initial concentration of metal ion used in adsorption process, the results simply reveal that increasing the initial concentration of metal ion leads to an increase in the metal uptake. Undoubtedly, it can be concluded based on this research that Tigernut activated carbon zeolite composite as a low-cost adsorbent will offer a lot of promising benefits for commercial purposes in the future.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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