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Efficacy of Groundnut Shell and Tea Leaves Waste on Adsorption of Chromium and Arsenic in Wastewater in Gombe Metropolis

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ABSTRACT

Heavy metals in water are the contaminants occurring from global industrialization and anthropogenic sources attributed to an inappropriate effluence disposal of the untreated wastewater form threats. Water pollutants can damage living organisms in the ecosystem. This study was aimed at using environmentally friendly permeable substance of groundnut shell and tea leaves (waste) in the removal of Cr and As heavy metals in contaminated water. which were determined from the Tumfure wastewater are above the permissible limits to reduce its menance. The sample adsorbents were characterized using AAS, SEM for concentrations, morphology and FTIR analysis that revealed the functional groups of alkohols, metabolites, aromatic and aliphatic hydrocarbons, also the result show effective Adsorption of Groundnut shell and Tea leaves Waste of range of 93 to 98 %. The metal ion concentrations analyzed was found to be; As = 27.26 mg/L and Cr =11.35 mg/L. An Adsorbent dose, contact time, effects of pH and temperature as thermodynamic parameters were studied in a batch which showed percentage removal for As and Cr ions in the water sample from Tumfure by the adsorbents showed 94.31% As and Cr = 95.95% with Groundnut shell whereas 96.55 % As = 98.09 % Cr with Tea leaves respectively. Batch adsorptions was also carried out on dosage which ranged from 0.2 - 1.0g, temperature which were varied at 25^{0c} - 60^{0c} C, contact time showed a range of 10 - 60 minutes and effect of pH were varied at 2 pH -10 pH respectively. The kinetic or adsorption process was tested to range between 0.04 t0 1 through pseudo first order and pseudo second order models. The Pseudo Second Order Kinetic Model provided the best correlation for experimental data for the two metals ions. Thermodynamics parameter, that's ΔG^0, ΔH^0 and ΔS^0 were also calculated which showed that the process of adsorption for ΔG^0 were negative showing spontaneity.

Keywords: Heavy metals, Wastewater, Adsorbents, Contaminations.

INTRODUCTION

Heavy metals are metallic elements with high atomic weight and density. These include the transition metals, some metalloids, lanthanides and actinides. Many reactive metals generally exist in a positively charged form and can bind on to negatively-charged organic molecules (Hui *et al*., 2005). As metals ions, heavy metals cannot be degraded or destroyed, therefore their stability makes them as the persistent toxic substances in environment. Heavy metals are the environmental contaminants components found in the air, soil and water, which pose health hazard to humans and ecosystem. (Wang *et al.,* 2013).

Presence of heavy metal in water as contaminants is an indication of global industrialization attributed to large scale of inappropriate disposal and untreated of wastewater containing heavy metal from anthropogenic sources (Wang *et al.,* 2013). Water functions as a medium of transport, it also carries some dissolved pollutants that can be damaging to both living organisms and the environment (Praveena *et al.*, 2008). Heavy metals can form bio-accumulated deposits over a period of time and their concentrations become apparent at measureable rates. Through food chains and trophic levels, heavy metals bio-accumulation also within target organ or tissue of organisms that can ultimately threaten human health. The maximum permissible limits for the discharge of heavy metals for survival in the aquatic environment are controlled. These contaminants, however, are the heavy metals which are being released at some higher concentrations than the prescribed limits especially through anthropogenic point source, thus leading to the health hazard and water pollution.

Heavy metals can be consumed by living organisms because of their high solubility in the marine environment. Large concentrations of heavy metals can accumulate in the human body once they reach the food chain. If the metals are ingested above the permissible concentration, they may cause serious health problems (Babel and Kurniawan, 2004). Domestic waste mostly has a lower level of heavy metals than industrial waste. Due to mass urbanization and the introduction of untreated industrial wastewater into municipal wastewater systems, hazardous metals can be found in municipal wastewater. Two classes of heavy metals can be classified on the basis of the relative toxicity to plants and animals. The first class that consists of chromium, cadmium, mercury, Arsenic and lead is extremely toxic to humans and animals but less toxic to plants. The second class comprising zinc, nickel and copper is more harmful to plants than to humans and animals when present in excess concentration (Gupta and Sen., 2017).

The current investigation focused on excess contaminants of waste water especially from congested urban area effluences of domestic usage. The application of locally improvised a porous adsorbent was adopted that remove the menace of these contaminants to the minimal level.

MATERIALS AND METHODS

Samples Collection

Sample of wastewater was collected from congested urban settlement effluences of domestic usage at Tumfure area of Gombe state Nigeria. The waste water sample was tested of its acidity or alkalinity using pH meter to determine the level of contamination. The sample waste water was mixed up vigorously that made it homogenized and then filled in plastic containers, then the process was done by inserting pH meter into a liter of the waste water collected from the contaminated area (Adenuga *et al*.,2019).

Collection of Groundnut Shell and Tea Leaves (waste) Sample

Groundnut shells was purchased at different parts of Gombe main market in Gombe State while the Tea Leaves was purchase from tea farm of Mambilla beverages Nigerian limited Kakara, Sardauna local government area of Taraba State, which are clean and heated with water to form extract that are filtered to obtained residue that serve as tea waste. The samples tea waste were used for the analysis as absorbent as adopted by Bratby, (2006)

Sample Preparation of Groundnut Shell and Tea Leaves (waste).

Groundnut shell (GS) and Tea Leaves (TL) waste were used as the raw material for the preparation of the adsorbents. The GS, and TL which was prepared from the items purchased from local markets and farm, were washed with distilled water several times to remove dust, adsorbed impurities and other contaminants. Samples of GS at 70 ^{0C} and TL waste at 93 ^{0C} were dried at room for two weeks separately inside a conservative oven for 25 - 30 min to remove any moisture left.

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Then the dried samples were crushed and sieved with 0.30 mm sieve that obtain smaller particles which are kept in a safer plastic bags that served as adsorbents prior to other treatment as adopted by Oliveira and Ayodele, (2004).

WasteWater Sample Preparation

The waste water from different sampling locations were prepared by filtering with filter cloth that remove bigger impurities, the filtrate was poured into a four liters' plastic container and kept un tempered for further analysis (Adenuga *et al*., 2019).

Batch Adsorption Process

Effect of the adsorbent dose on Sample Waste Water

Different amount of dosage of 0.2, 0.4, 0.6, 0.8, and 1.0g of the adsorbents (Groundnut Shell and Tea leaves waste) were measured and added to 10 beakers containing 50 ml wastewater, five samples of each adsorbent with the initial concentrations of 27.26 mg/L of As metal from Tumfure waste water and 11.35 mg/L of Cr metal from Tumfure waste water. Then the samples were shaken for 30 minutes at 150 rpm in an Orbital shaker at a constant temperature of 25^{0C} until it was separated into layers. Then the solution was filtered using whatman No1 filter paper and the filtrate was used to analyzed high concentrations of heavy metals content (Adenuga *et al*., 2019).

Effect of temperature on the adsorption

Effect of temperature on wastewater on the adsorption process of As and Cr ions was studied at the following temperature 25, 30, 40, 50 and 60°C. 1g of the adsorbent dose (Groundnut shell and Tea leaves) were transferred into 10 beakers containing 50ml of the wastewater five each for the two sample adsorbents. The solutions were shaken at 150rpm at different temperatures, contact time of 30min. The solutions were filtered using whatman No1 filter paper and the filtrate was used to analyzed high concentrations of heavy metals content (Adenuga *et al.,* 2019).

Effect of Contact Time.

Effect of contact time on the adsorption process of As and Cr ions was investigated using Groundnut Shell and Tea Leaves waste were analyses at a specific time intervals range of 10 to 60 minutes with an adsorbent dose of 1.0 g were added to each of 10 beakers containing 50 ml of the wastewater, they were then shaken at 150 rpm at different time intervals taken to an orbital shaker at room temperature of 25^{0C}. The solutions were filtered using whatman No1 filter paper and the filtrate was used to analyzed high concentrations of heavy metals content as adopted by Adenuga *et al.,* (2019).

Effect of pH on the Adsorption

Different pH value range from 2 to 10 at interval of 2 each with the same initial concentration of metal As and Cr of 13.83mg/L , were determined at room temperature of 25^{0C}. The pH was adjusted by pouring 2 ml of 0.1M NaOH and 0.1m HNO_3. into 50 ml of wastewater. The mixture was blended into 10 beakers containing 1.0 g of Groundnut Shell and Tea leaves waste. Five beakers each for the two adsorbent and was shaken for 30 min at 150rpm using an Orbital shaker. The solutions were filtered using whatman No1 filter paper and the filtrate was used to analyzed the amount high concentrations of heavy metals content absorbed (Adenuga *et al.,* 2019).

RESULTS AND DISCUSSION

Effect of Adsorbent Dosage in Tumfure Water Water

Variable dosages of adsorbents at interval of 2 range from 0.2 g to 1.0 g were used under an identical pH condition of 7, were determined

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from the wastewater as indicated on Figure 4.1. The result showed that an increase in absorbent dose from 0.2 g to 1.0 g on Cr ion corresponds to increase in removal of high concentrated ions in the waste water from 95% to 98 %. The efficacy is the same with As metal but the percentage removal of metal change from 94 % to 97 %. Similar trend was shown by effect on variation of adsorbent dose was emanated (Lawan *et al.,* 2010).

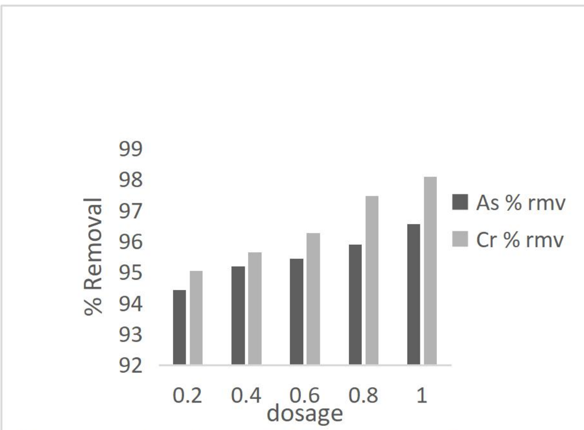

Figure 1: % of As and Cr remove by Tea Leaves waste in Tumfure water

Figure 2 showed the efficacy of Groundnut shell adsorbent on percentage removal of high concentration heavy metals ions of As and Cr ions in Tumfure waste water. The result showed that an increase in absorbent dose from 0.2g to 1.0g on Cr ion corresponds to increase in removal of high concentrated ions in the waste water from 93 % to 96 %, while The trend of removal effect is the same with As ions but the percentage removal of ions changes from 93 % to 95 %.

The surveillance effect is synonymous to an increase in the available binding sites on the heavy metal ions due to the increase in the surface area of the adsorbent associated with increased dosage as reported by (Lawan *et al.,* 2010). This is also paramount to the amount of adsorbent that was added corresponded to the more available adsorptions sites are increased which directly increases the rate of adsorption of metal ions.

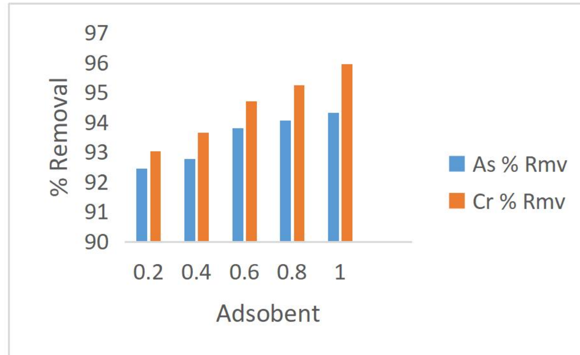

Figure 2: % Effect of adsorbent dose on As and Cr metals by Groundnut Shell in Tumfure water

Effect of Contact time on Groundnut shell and Tea leaves waste

Adsorption of both As and Cr ions were studied under a variable contact time range from 10 to 60 min at interval of 10 minutes each using the optimized amount of 1.0 g of both adsorbents at a constant pH value of 7. The result obtained in Figure 3 shows Cr ions display steady increase adsorption removal of these ions starting 85 % to 97 % at 60 minutes, while As ions shows progressive adsorption range from initial 10 minutes of 90 % to final 60 minutes of 97.5 % removal of high concentrated ions in the waste water. At the end a saturation point was reached and equilibrium was established between the adsorbed metal ions and the remaining metal ions in the solution as adopted by Nyoni *et al*.,(2017). Renu and Singh (2017) reported that at varying contact time of 2 minutes only 18 % removal of Cr was possible while at higher contact time of 10 to 60 minutes 88% removal of metals was achieved.

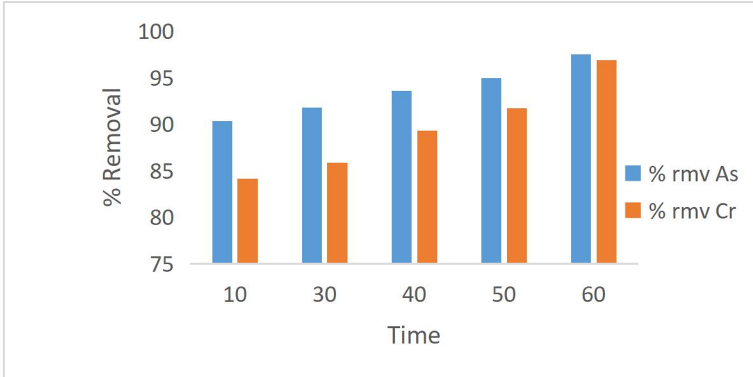

Figure 3: Effect of contact time in absorption of As and Cr by Tea leaves in Tumfure water

Figure 4 shows a slight progression in the removal of metal ions as the time increases from 10 minutes to 60 minutes. Both As and Cr ions were adsorbed under a variable contact time range from 10 to 60 min at interval of 10 minutes each using the optimized amount of 1.0 g of both adsorbents at a constant pH value of 7. The result obtained in Figure 4 shows As metals displayed steady increase absorption removal of these ions starting 92 % to 94 % at 60 minutes, while Cr metals also shows steady absorption range from initial 10 minutes of negligible less than 1% to final 60 minutes of 97.8 % removal of high concentrated ions in the waste water. The result obtain was contrary to the findings of Renu and Singh (2017) were contact time was fluctuating at different time interval.

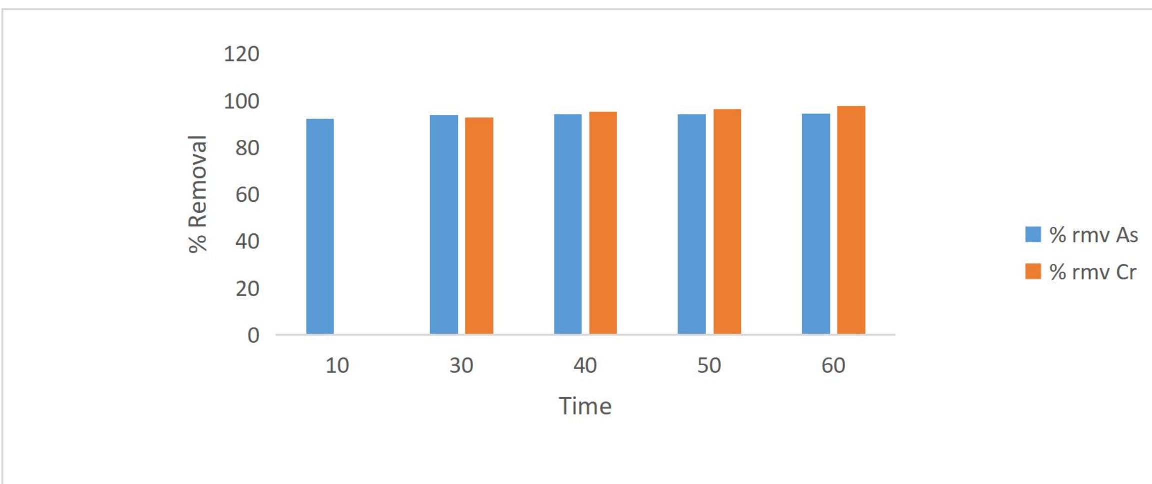

Figure 4: Effect of Contact time on adsorption of As and Cr by Groundnut Shell in Tumfure water

Effect of Temperature on Groundnut shell and Tea Leaves Waste

The temperature has strong effects on the intermolecular forces between the adsorbate and adsorbent particles. Figure 5 showed that there was a progressive increase in adsorption of both metal ions as the temperature increases. The result shows As metals display gradual increase absorption removal of these ions starting 94.8 % to 98.8 % at 60 minutes, while Cr ions also shows steady absorption range from initial 10 minutes from 96% to final 60 minutes of 99 % removal of high concentrated ions in the waste water. The result obtained on percentage removal ranges from 96 % to 99 % which was contrary to the result reported by Renu and Singh (2017) with range between 70 % to 93 % removal using different organic and inorganic adsorbent

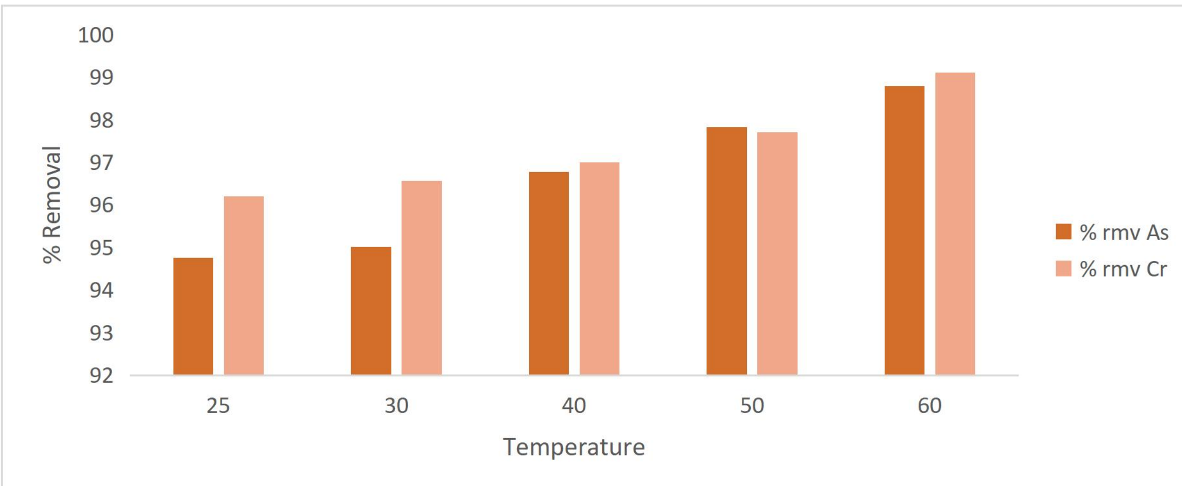

Figure 5: Effect of Temperature on adsorption As and Cr by Tea Leaves Tumfure water

Figure 6 showed that there was a progressive increase in adsorption of both metal ions as the temperature increases. The result shows As metals display gradual increase absorption removal of these ions starting 91 % to 95 % at 60 minutes, while Cr ions also shows steady absorption range from initial 10 minutes from 96% to final 60 minutes of 98 % removal of high concentrated ions in the waste water. The result obtained was synonymous to the findings of Adebayo *et al*., (2012) but contrary to the findings of Renu and Singh (2017) using cigarette filter and graphene at a variable temperature 10^{0C} to 40^{0C}showing only 63% to 79% removal.

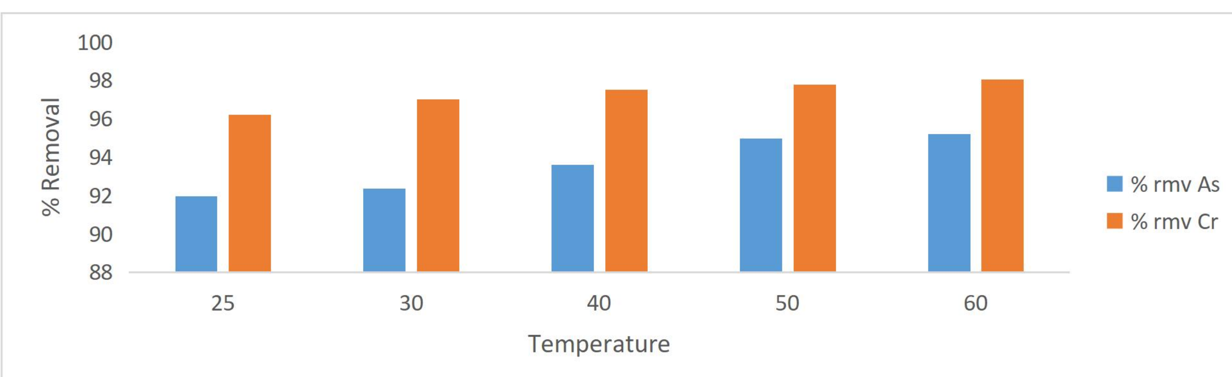

Figure 6: Effect of Temperature on adsorption of As and Cr by Ground Shell in Tumfure water

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pH values in Adsorbent Filtrate of Tea leaves waste and Groundnut Shells.

The pH of the metal ion solution is a critical variable in the adsorption process of metal ions from aqueous solution. Figure 7 shows electrostatic bonding between hydrogen ions and metal ions for the active binding sites that influence of pH ionization of functional groups on the adsorbent surfaces, of the metal ions. The effect of the pH of the adsorption As metals shows small adsorption range from initial 10 minutes of 98 % to final 60 minutes of 99 % removal of high concentrated ions in the waste water while Cr ions also shows steady absorption range from initial 10 minutes from 97 % to final 60 minutes of 99 % removal of high concentrated ions in the waste water. The result obtained was synonymous to the investigations of (Amuda , 2007), however, Renu and Singh (2017) investigated the percentage removal by varying pH of less than 2 using oxidized multi- wall carbon nanotube achieved 100% removal while Nitric acid carbon nanotubes showed only 18 % removal Cr ions.

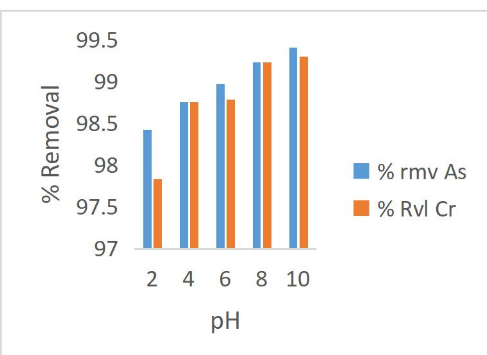

Figure 7: Effect of pH adsorption of As and Cr by Tea Leaves waste in Tumfure water

Figure 8 shows the effect of the pH of the adsorption As ions shows fluctuating adsorption range from initial 10 minutes of 96 % to final 60 minutes of 97 % removal of high concentrated ions in the waste water while Cr ions also shows steady absorption range from initial 10 minutes from 93 % to final 60 minutes of 97 % removal of high concentrated ions in the waste water. The result obtained was synonymous to the investigations of (Amuda , 2007)

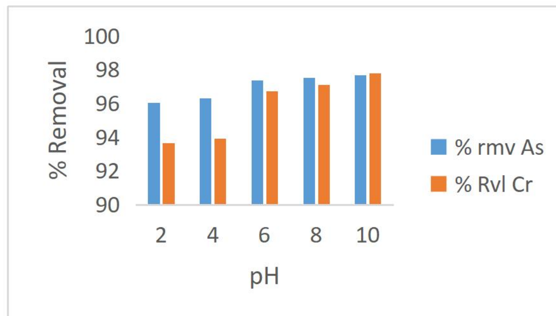

Figure 8: Removal of As and Cr by Groundnut Shell in Tumfure water

Absorption Kinetics

Figure 9 indicated R^2 value for As Groundnut shell Tumfure water showed pseudo first order with a value of 0.4088 when a graph of time verses kinetics was plotted, while Figure 10 showed that of second order for Groundnut shell As in Tumfure waste water have a value of 1 as kinetics values was computed. Lagergren's pseudo-first-order and Ho's pseudo-second-order models were applied to the experimental data in order to clarify the adsorption kinetics of As and Cr metal ions. The result obtained is contrary to Ahmed *et al*., (2020) which shows R^2 value= 0.649 for pseudo first order model while 0.988 R^2 value was obtained for second order.

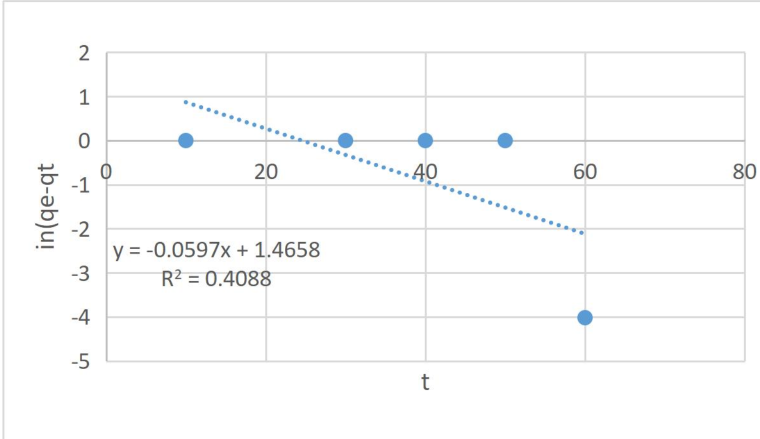

Figure 9: Pseudo First Order for As ion Groundnut Shell Tumfure

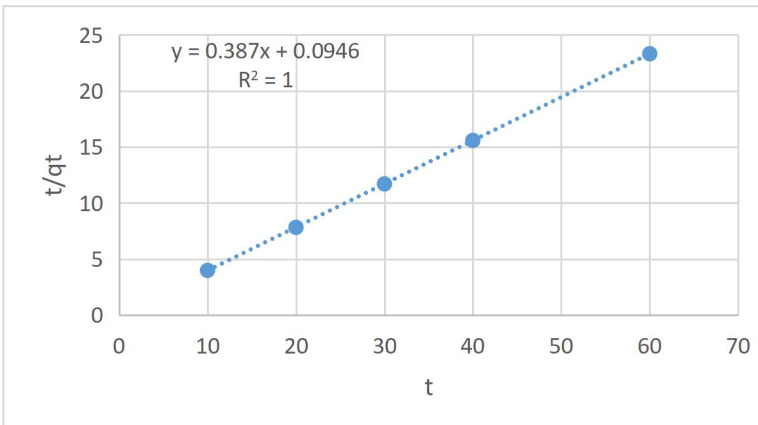

Figure 10: Pseudo Second Order for As ion Groundnut Shell Tumfure

Figure 11, showed the R^2 value for pseudo first order for Cr Groundnut shell Tumfure waste water was calculated as R^2 value of 0.9676 whereas, for second order, as shown in Figure 4.12 R^2 value for pseudo first order for Cr Groundnut shell at R^2 value of 0.9996.

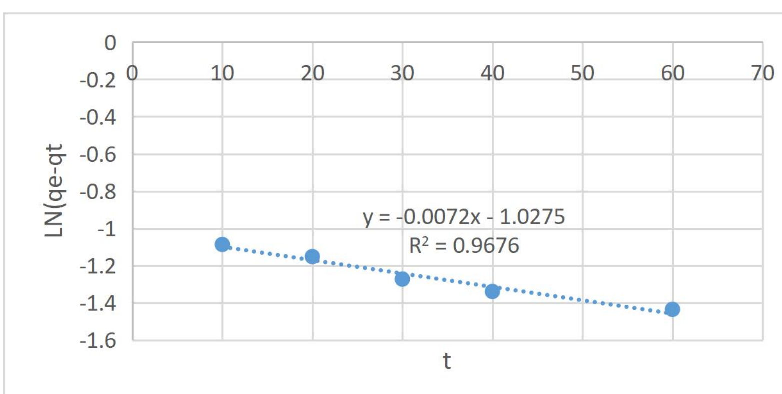

Figure 11: Pseudo First Order for Cr Groundnut Shell Tumfure

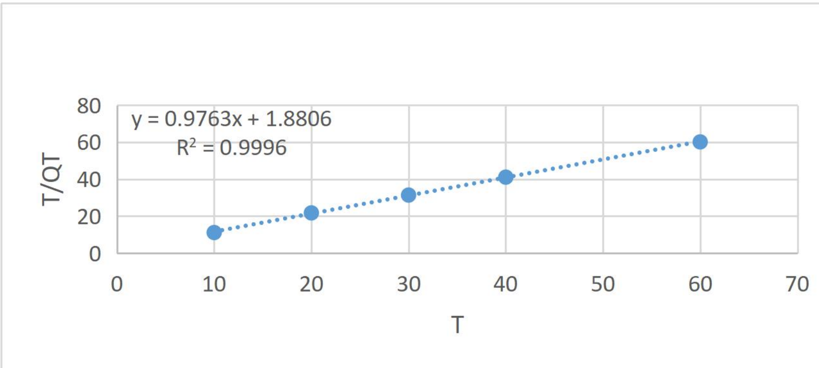

Figure 12: Pseudo Second Order for Cr Groundnut Shell Tumfure

Figure 13 showed R^2 value of 0.8589 for As Tea leaves in Tumfure water for pseudo first order model whereas Figure14 showed R^2 value of 1 As metal in Tea leaves of Tumfure water pseudo second order.

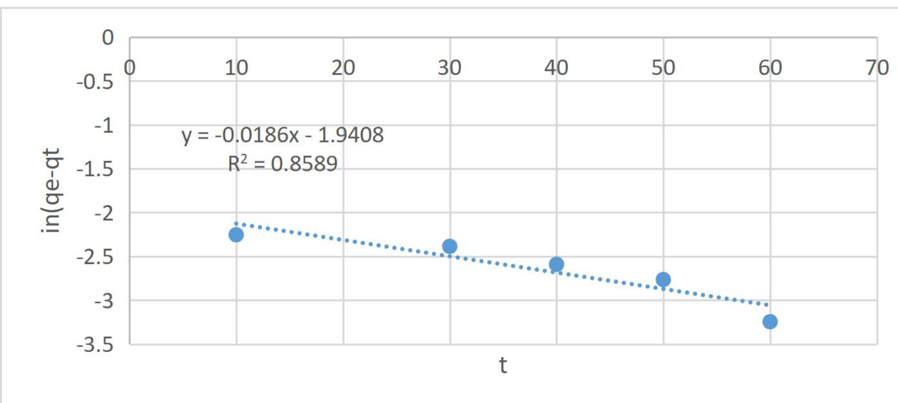

Figure 13: Pseudo First Order for As ion Tea Leaves waste of Tumfure

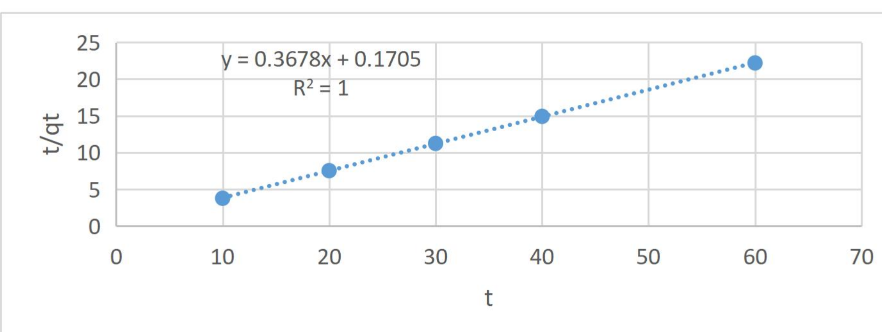

Figure 14: Pseudo Second Order for As Tea Leaves waste of Tumfure

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Figure 15 showed R^2 value for pseudo first order Cr Tea leaves in Tumfure water was recorded as 0.9676. Figure 16 showed the R^2 value for Cr Tea leaves waste in Tumfure waste water showed pseudo second order of 0.9547. This results obtained revealed that, the pseudo-second-order model R^2 value for the absorption of As and Cr ions in wastewater is higher than R^2 value for pseudo-first-order-model. This implies that the pseudo-first-order model is not efficient in the concepts of the kinetics of the adsorption of the metals. Hence, the pseudo-second-order model is more efficient and significant in the observed rate. This suggests that sorption of the metal ions involve two species, the metal ion and the biomass. The results investigated on maximum adsorption capacities for metal ions adsorption with different adsorbents which is synonymous to the several natural sorbents work done by (Chiou and Li, 2003). The result obtained is contrary to Ahmed *et al*., (2020) where Pb and Cu ions were removed showed R^2 value= 0.649 for pseudo first order model while 0.988 R^2 value was obtained for second order.

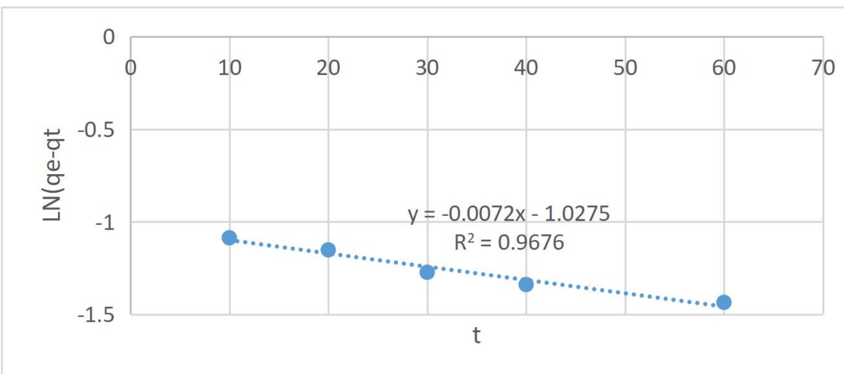

Figure 15: Pseudo First Order for Cr Tea Leaves waste of Tumfure

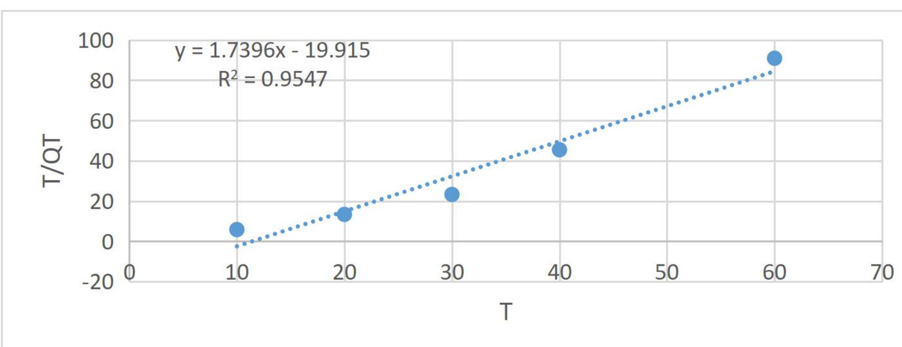

Figure 16: Pseudo Second Order for Cr Tea Leaves waste of Tumfure

Adsorption Thermodynamics

The thermodynamic data obtained from the adsorption of As and Cr metal ions by Groundnut Shell and Tea Leaves from wastewater are plotted. Figure 17 to Figure 20. The negative values of ΔG, implies that the adsorption of the metal ions are spontaneous and feasible. At some point the ΔG value also decreased in magnitude with increasing temperature for the metal ions. As observed in

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this research, the adsorption process gave positive values for ΔH and ΔS. A positive enthalpy (ΔH) indicates that the adsorption process was endothermic for the metal. From the magnitude of the adsorption enthalpy of the metal ion, there is the possibility of a moderately strong bonding between the adsorbate and the adsorbent. A positive change in the entropy is an indication of an increase in randomness at the solid–liquid interface during the adsorption of the metals, it also suggests some structural changes in the adsorbate and the adsorbent. Similar trend was made by (Lawan *et al.,* 2010).

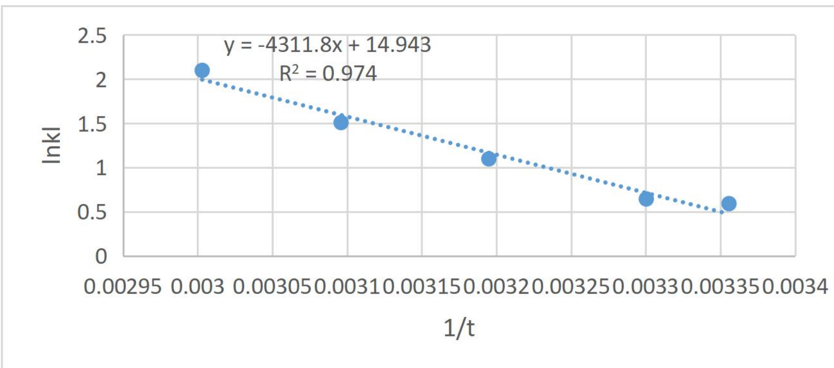

Figure 17: Thermodynamic for As ion using Tea Leaves waste on Tumfure waste water

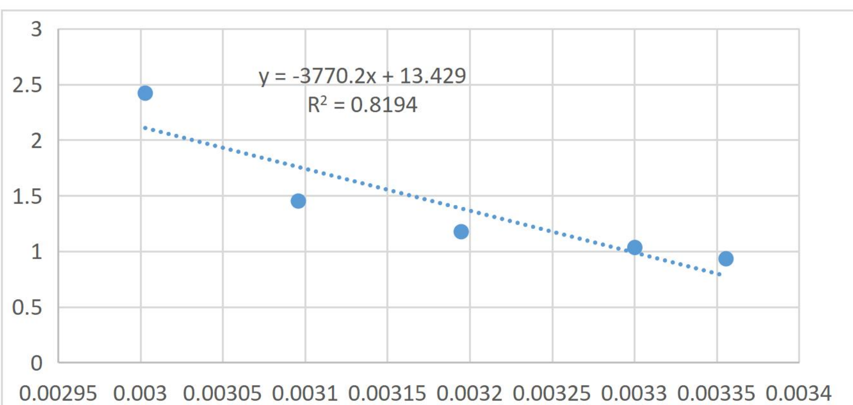

Figure 18: Thermodynamic for Cr Tea Leaves waste of Tumfure

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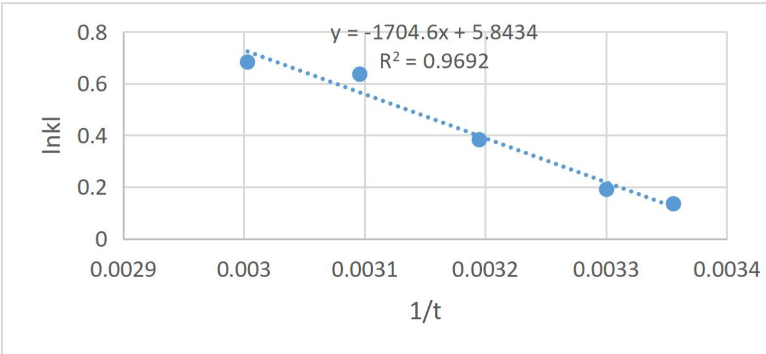

Figure 19: Graph of thermodynamic for As Groundnut Shell Tumfure

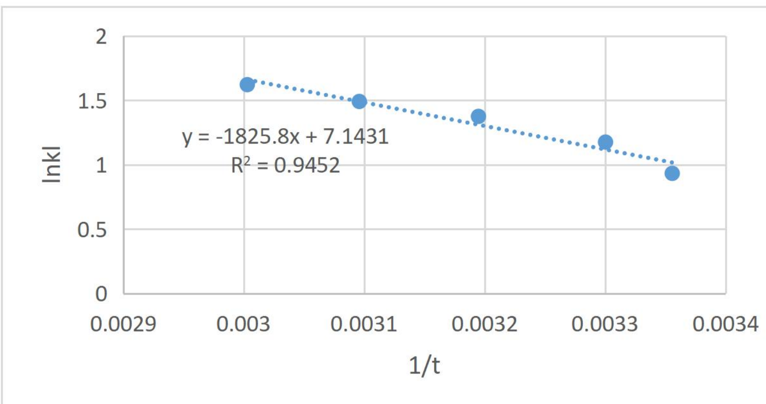

Figure 20: Thermodynamics for Cr Groundnut Shell Tumfure

CONCLUSION

In this study, Groundnut Shell and Tea leaves waste were used for adsorption process that removed highly concentrated heavy metals ions of As and Cr from wastewater. The adsorption performance of As and Cr are significantly affected by adsorbent mass, contact time, pH, temperature and concentration. Investigations on the efficiency of the Tea Leaves waste and Groundnut shell in adsorption of heavy metals was paramount on Tumfure waste water, were Tea leaves waste was more efficiency than Groundnut Shell in adsorption. The maximum adsorption efficiencies for heavy metal ions were found to be As = 98.19 % and Cr = 98.50 % using Tea Leaves waste on Tumfure waste water. Whereas, As = 98.19 % and Cr = 96.87 % using groundnut shell respectively. The ANOVA results at 95% confidence level suggest that there were no significant differences in the mean concentration of the two heavy metals. Adsorption efficiency of As and Cr ions on Tea Leaves waste was slightly faster and more efficient than adsorption of heavy metals using Groundnut Shell. This study showed high adsorption efficiency of the heavy metals using easy and simple water treatment process by utilizing inexpensive adsorbents. However, result investigated was a through efficacy of porous nature of the two adsorbent used that systematic regulate high percentage of excess harmful concentrations of heavy metals study

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is required. The kinetics studies also indicated that the adsorption process of the metals ions followed the pseudo second-order model with R^2 value of 0.9998 As = 0.9996 and Cr = 0.9997 of Groundnut shell of Tumfure waste water, while As = 0.997 and Cr = 0.9547 of Tumfure Tea Leaf waste respectively. The advantage of high metal adsorption of the biomass Groundnut shell and Tea Leaves waste has greater potential to be used as a simple, efficient, effective and at minimal cost adsorbent material for the adsorption of Cr and As ions from waste water.

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