Comparative Kinetic Study of the Adsorption Capacity of Walnut shell and its biochar for Chromium Removal fromWastewater

ABSTRACT

Chromium is a toxic heavy metal that can pollute water from industrial and agricultural activities. Adsorption is a promising method for removing chromium from wastewater, and walnut shell is a sustainable and abundant biomass that can be used to produce biochar for adsorption. This study compares the effectiveness of walnut shell and walnut shell biochar for chromium removal from wastewater using adsorption. The effects of various parameters on chromium adsorption, such as pH, biochar dosage, and contact time, are investigated. The results show that both walnut shell and walnut shell biochar are effective adsorbents for chromium removal. However, walnut shell biochar exhibits a higher adsorption capacity and faster adsorption kinetics than walnut shell. The findings of this study suggest that walnut shell biochar is a promising adsorbent for chromium removal from wastewater. It is a sustainable and low-cost material that can be used to develop effective and efficient wastewater treatment systems.The kinetics of Cr adsorption will examine using pseudo-first-order, pseudo-second-order, and adsorption isotherms. The results demonstrated that the adsorption of Cr onto WS and BC followed pseudo-second-order kinetics, suggesting chemisorption as the rate-limiting step.

Keywords: Nanotechnology, Walnut shell,Biochar, Adsorption,Kinetic and Equilibrium modeling.

1. INTRODUCTION

Water pollution is the contamination of water bodies with harmful substances that make the water unsafe for drinking, swimming, and other activities[1]. It can be caused by a variety of sources, including industrial and agricultural runoff, sewage, and storm water[2]. Water pollution can have a devastating impact on human health and the environment[3]. It can cause a variety of diseases, including cholera, typhoid, and dysentery[4]. It can also kill fish and other aquatic life, and damage ecosystems.There are a number of things that can be done to reduce water pollution[5]. These include: Treating wastewater before it is discharged into rivers and lakes, reducing the use of pesticides and fertilizers in agriculture, managing stormwater runoff, conserving water. Water pollution is a serious problem, but it is one that can be solved. By taking steps to reduce water pollution, we can protect our health and the environment for future generations[6].

Chromium is a heavy metal that is naturally found in the Earth's crust[7]. It is used in a variety of industrial and commercial applications, such as plating, metal finishing, and leather tanning[8]. However, chromium can also be a toxic metal, especially in its hexavalent form (Cr(VI) [9].Chromium pollution can occur when chromium-containing wastewater is discharged into the environment without proper treatment[9]. This can happen from a variety of sources, including industrial facilities, electroplating plants, and tanneries[10]. Chromium pollution can also occur from natural sources, such as volcanic eruptions and the weathering of chromium-bearing rocks[11].Chromium pollution can have a negative impact on human health and the environment. Chromium exposure can cause a variety of health problems, including skin irritation, respiratory problems, and cancer. Chromium can also be toxic to aquatic life and can damage ecosystems[11].

There are a variety of methods that can be used to remove chromium from wastewater[9]. These methods include chemical precipitation, ion exchange, and adsorption[12]. Adsorption is a particularly promising method for chromium removal because it is relatively simple and inexpensive.Adsorption involves the use of a solid material, called an adsorbent, to attract and bind chromium ions from the wastewater[13]. A variety of materials can be used as adsorbents, including activated carbon, biochar, and metal oxides[14].Once the chromium ions have been adsorbed onto the adsorbent, the adsorbent can be removed from the wastewater[14]. This can be done by filtration, sedimentation, or other separation techniques.Adsorption is a cheap and effective method for chromium removal[15]. It is also a versatile method that can be used to remove chromium from a variety of wastewater streams[16].

Here are some examples of low-cost adsorbents [17]that can be used for chromium removal:Agricultural wastes, such as rice husk, wheat straw, and banana peels, Industrial wastes, such as fly ash and red mud and Natural materials[18], such as clay and zeolites[19]. The adsorption method is a promising and sustainable approach for chromium removal from wastewater[20]. It is a cheap, effective, and versatile method that can be used to remove chromium from a variety of wastewater streams[15].

Farming waste materials, for example, rice grain, rice husk, wheat grain, wheat husk[21], tree rind, nutshell, pecan shell, coconut shells[22], Aloe vera extricate, green tea leaves, maize corn cob, sugarcane bagasse, apple strip, banana strip, orange strips[23], soybean bodies, grape stalks, espresso beans, and others have been named as bio-adsorbents. These promising horticultural waste materials are used to eliminate metal particles in their local state or after some physical or substance treatment[24].The capacity, affinity, and specificity of the waste material, as well as its physicochemical constitution, determine its efficiency[25]. Different biosorbents have been contemplated to wipe out the metal particles like chromium, nickel, cadmium, mercury, copper, lead, arsenic ,and others[26].

An arrangement of cultivating wastes, similar to orange strips, maize cobs, nutshells, and soybean outlines, have been inspected in customary and changed structures, with basic departure viability recorded[27]. Different plant parts, for instance, coconut fiber quintessence, coconut shell fiber, pine needles, desert vegetation leaves, and neem leaf powder, have furthermore been pursued for chromium clearing, with results going from 90% to 100% at ideal pH[28]. At an ideal pH of 6.0, the use of rice grain and wheat grain as an adsorbent achieved a 90 percent ejection capability of Cr VI[29]. For the departure of chromium (VI), normal rice husk as well as started rice husk carbon was utilized, and the results diverged from business incited carbon and various adsorbents[30].

Agricultural wastes such as rice straw, sugarcane bagasse, soybean frames, nut shells, and pecan shells in their normal state have been noticed to remove 98 percent of lead[31]. For the elimination of lead, agricultural waste of dark gram husk, blossoms of Humuluslupulus, squander tea leaves, and water hyacinth were tested , and their efficiency was ranged from 70 to 98 percent.The expected utilization of rice grain and wheat for cadmium sequestration was investigated, and substantial removal efficiency was found. Studies on the removal of cadmium using rice polish, rice husk, and black gram husk in their native and modified forms were also undertaken, and their general adequacy was accounted for. The cortex of plants like Pesciaglehnii has been used to remove cadmium. Other plant components used as adsorbents, such as pea strips, fig leaves, expansive beans, orange strips, and jack natural products, have shown high evacuation viability at acidic pH. Adsorption tests on nut structures, pecan shells, and green coconut shells yielded significant cadmium evacuation results[24].

Biochar is a solid made by pyrolyzing biomass at temperatures below 700°C in the absence or low presence of oxygen[32]. The resultant material has greater carbon content and has good surface assimilation properties, thus it can remove regular and inorganic toxic substances from polluted water[33]. Different waste things, like straw, countenances, and muck, have been assessed as biochar source. It has been demonstrated that biochar may be produced using several processes like pyrolysis[34], gasification, and fluid carbonization. Preparation of biochar can be affected by the sort of natural materials feedstock, the planning temperature, and change strategies.Sawdust is a type of agricultural waste that can be used to remove colors, harmful metals, and salts from wastewater[35]. Numerous particles (like cellulose, and hemicellulose, lignin) and polyphenolic bunches are available in this material, and they assume a significant part in restricting to natural mixtures through different components, for example, particle trade, complexation, and hydrogen holding. Similarly, the efficacy of agro-waste walnut shell biochar adsorbent in removing nickel and lead from wastewater has been documented[36].

Electrostatic interaction, ion exchange, pore filling, and precipitation can all be used to explain how biochar removes organic and inorganic contaminants. This is dependent on the biochar's physicochemical properties, such as dosage, pyrolysis temperature, and medium/effluent pH[37]. Another way to use biomass for wastewater treatment is to use it as a substrate for microorganisms. Microorganisms can be used to break down organic matter in wastewater and to remove nutrients, such as nitrogen and phosphorus. Biomass can be used to create biofilters, which are systems that contain biomass and microorganisms. Wastewater is passed through the biofilter, where the microorganisms break down the pollutants [38].

Biomass can also be used to generate energy for wastewater treatment plants[39]. For example, biogas can be generated from anaerobic digestion of biomass. Biogas can then be used to generate electricity or heat. Biomass is being used for wastewater treatment throughout world such as in the United States, the city of San Diego is using biochar to remove pollutants from wastewater effluent. The biochar is produced from agricultural waste, such as rice straw and wheat straw.In the Netherlands, the company Royal HaskoningDHV is using biofilters to remove nutrients from wastewater[40]. The biofilters are filled with wood chips and other biomass materials.In India, the company Envitech is using biogas generated from anaerobic digestion of biomass to power a wastewater treatment plant.The use of biomass for wastewater treatment is a promising and sustainable approach. Biomass is a renewable resource that can be used to produce adsorbents, substrates for microorganisms, and energy. The use of biomass can help to reduce the cost of wastewater treatment and to improve the quality of treated wastewater.

Walnut shell is a promising biomass for wastewater treatment due to its high carbon content, porous structure, and abundance[41]. Walnut shell biochar can be produced by pyrolyzing walnut shell at high temperatures in the absence of oxygen. Biochar is a charcoal-like material with a high surface area and a variety of functional groups, which makes it an effective adsorbent for pollutants in wastewater.Walnut shell biochar has been shown to be effective in removing a variety of pollutants from wastewater, including heavy metals, dyes, and organic matter. For example, a study found that walnut shell biochar could remove 99% of lead from wastewater. Another study found that walnut shell biochar could remove up to 95% of the dye methylene blue from wastewater[42].

Walnut shell biochar can be used in a variety of ways to treat wastewater[43]. It can be used as a packing material in biofilters, or it can be added directly to wastewater. Walnut shell biochar can also be immobilized on other materials, such as sand or gravel, to create composite adsorbents. Walnut shell biochar is being used for wastewater treatment such as in China, walnut shell biochar is being used to remove heavy metals from wastewater from a mining operation.In India, walnut shell biochar is being used to remove organic matter from wastewater from a textile mill.In the United States, walnut shell biochar is being used to remove dyes from wastewater from a printing and dyeing plant.The use of walnut shell biochar for wastewater treatment is a promising and sustainable approach. Walnut shell biochar is an effective adsorbent for a variety of pollutants, and it can be produced from a renewable resource. The use of walnut shell biochar can help to reduce the cost of wastewater treatment and to improve the quality of treated wastewater[43].

2. METHODOLOGY

2.1Preparation ofMaterial

About 2kg of Walnuts were purchased from the local market. Their shells were collected and then washed through tap water to clean them with dust particles and to remove pollutants, the shells were rinsed With distilled water again. The washed shells were dried in the shade to ensure that all of the moisture in the shells was gone. To make powder, the dried shells were crushed and the ground by pestle and morter. The powder was stained with the help of nanoseive to convert it into nano biomass. To prepare biochar in the current research, the walnut shell powder was pyrolyzed in a retort heater at 500 c for 4 hours. The obtained biochar was ground with a pestle and mortar and then sieved with the help of a nanoseive to obtain nano-biochar.

Fig. 1 Preparation of nano biomass(a,b,c,d) and nanobiochar(e,f)

2.2 BATCH ADSORPTION

To set up a 1000ppm stock arrangement of chromium, 2.8289g of potassium dichromate was broken up in 1000ml refined water. To set up the 1000ppm stock arrangement of cadmium, 2g of chromium salt was disintegrated and was put in a 1000ml round bottom flask. Adsorption tests were carried out to determine the removal efficiency of Biomass(BM) and Biochar(BC) for chromium. Working solutions of 50ppm in 2000ml distilled water were prepared from stock solutions using the dilution formula($C_1V_1=C_2V_2$). For the pH adjustment of working solutions, 0.1M HCl and 0.1M NaOH were prepared. Different parameters of dose rate, concentration, pH, and contact time were applied to investigate the adsorption of chromium. Adsorption tests were performed by taking 100ml of working solution with specific pH in 250ml conical flasks. All the conical flasks with samples were placed in an orbital shaker for 2 hours at the speed of 130rpm. The dose rate effect was investigated with all adsorbents doses of 0.05g, 0.1g, and 0.15g.0.2g, 0.25g. For chromium adsorption, pH effect was observed at pH of 1,2,3 and 4. Initial concentrations were also varied at 10ppm, 25ppm, 50ppm, 100ppm, 200ppm, 400ppm. Contact time was varied at the interval of 0sec and 15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, 1440 minutes.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF BIOMASS AND BIOCHAR

3.1.1 FTIR Analysis

The FTIR spectra of walnut shell and biochar at different pyrolysis temperatures are given here. The examination gives data on the compound synthesis of the substance as well as a few natural and inorganic functional groups. Somewhere in the range of 3600 and 3100 cm^{-1}, O-H extending vibrations recommend the presence of phenols, alcohols, and carboxylic corrosive. The presence of this wideband with hydrogen holding recommends that there was still some water in the shell. With expanding temperature, at 600 °C, water content nearly disappears. The presence of alkanes is shown by C-H extending groups somewhere in the range of 3000 and 2800 cm^{-1} and C-H deformity groups somewhere in the range of 1350 and 1475 cm^{-1}. The presence of aldehyde, ketones, and carboxylic acids is shown by CO carbonyl vibrations with conveyance groups somewhere in the range of 1750 and 1625 cm^{-1}. The presence of amides is demonstrated by groups somewhere in the range of 1640 and 1550 cm^{-1}. A few groups in the scope of 1800 to 900 cm^{-1} are responsible for cellulose, hemicellulose, and lignin. C extending vibrations are in the range of 1575 and 1675 cm^{-1}. In ethers and esters, C-O extending vibrations happen somewhere in the range of 1300 and 1000 cm^{-1}. At the point when the pyrolysis temperature is raised, the strength of a few bonds diminishes. Many peaks are missing, indicating that the char is carbonized in general. Many creators believe that as the temperature rises, the aromatic substance expands as well [44].

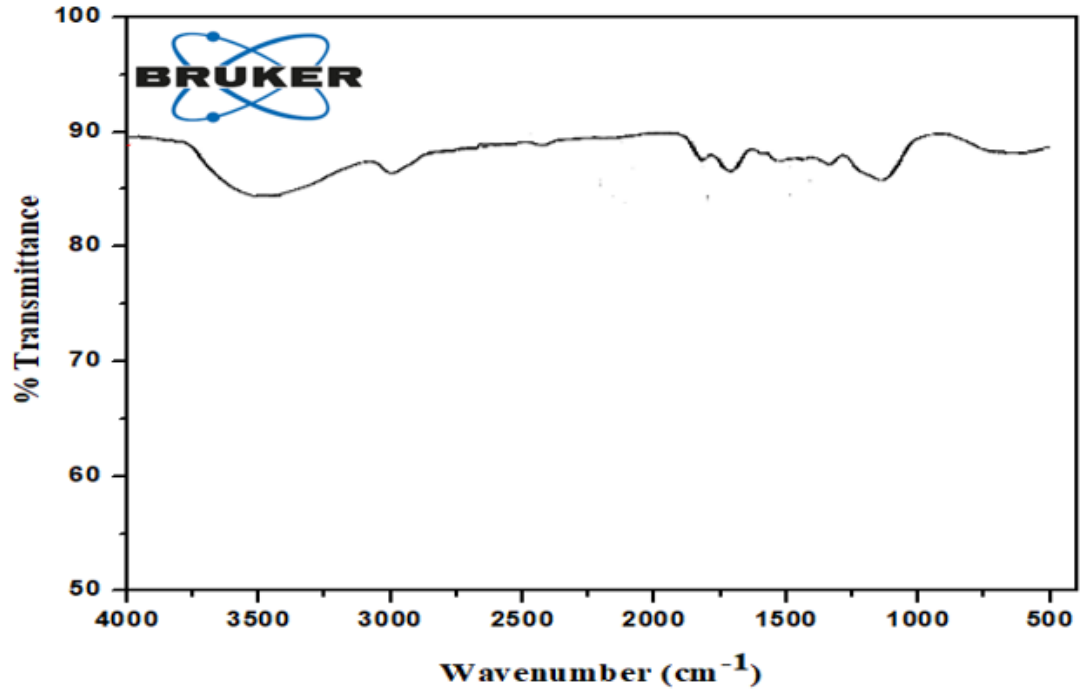

Fig.2 Graphical presentation showing transmittance (%) of Raw Walnutshell

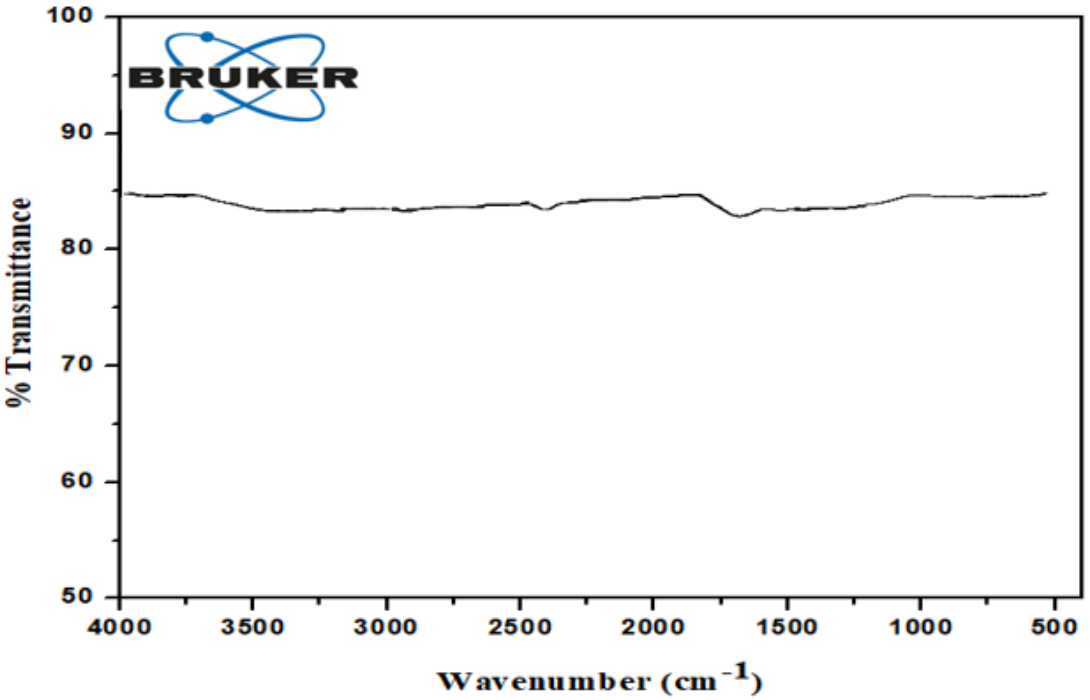

Fig. 3Graphical presentation showing transmittance (%) of biochar at 300˚C

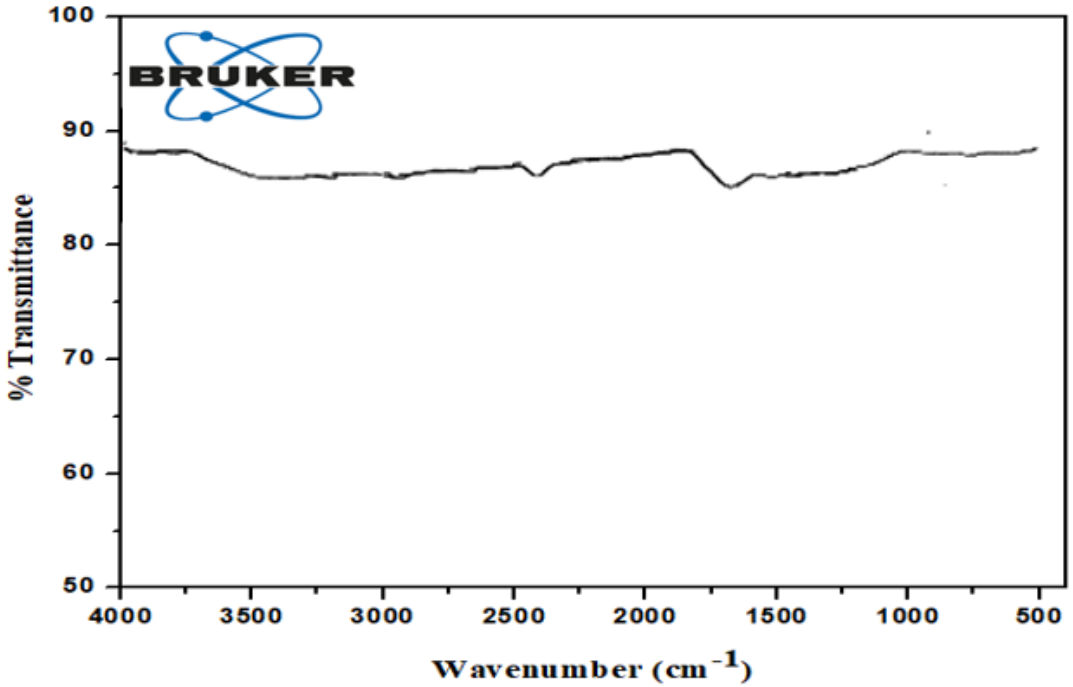

Fig. 4Graphical presentation showing transmittance (%) of biochar at 400˚C

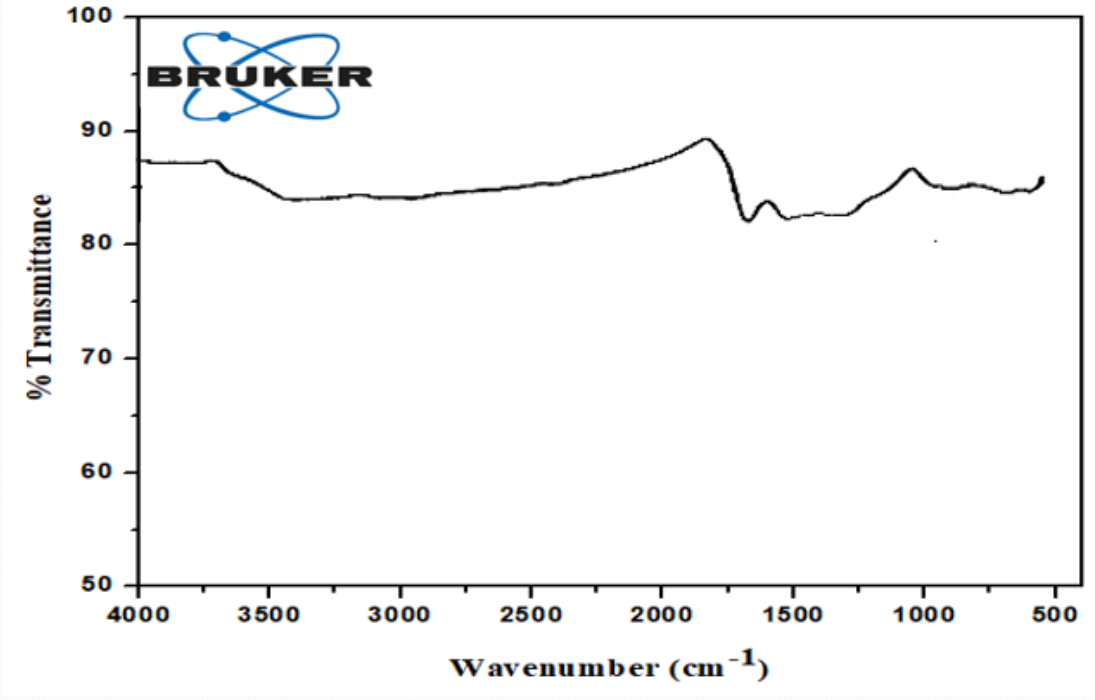

Fig. 5Graphical presentation showing transmittance (%) of biochar at 500˚C

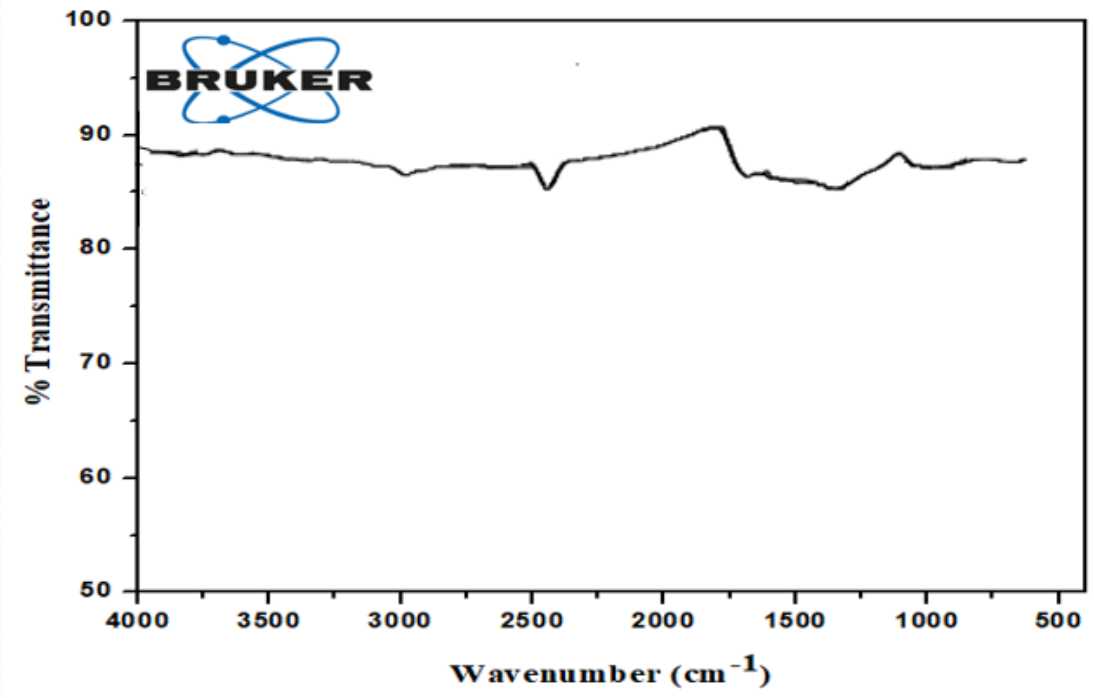

Fig. 6Graphical presentation showing transmittance (%) of biochar at 600˚C

3.2Effect of pH

The adsorption mechanism is heavily influenced by the pH of the solution. At different pH values, the pollutant may act differently, and functional groups on the adsorbent surface may operate differently as well. This, in turn, affects adsorption efficiency by altering the surface charge density of the adsorbent, potentially disrupting analyte-adsorbent interactions. The pH of the adsorbent surface is determined by the functional groups present. Protonation is often carried out at a low pH, resulting in an electrostatic attraction between the surface adsorbent and the metal for removal.
Protonation and deprotonation of the groups present at the surface of the adsorbent govern the surface charge density when the pH changes.Using certain adsorbents such as walnut shell biomass and its biochar, the impact of pH on the adsorption of chromium was investigated in this study. The current study looked into whether adsorption is greatest at optimal pH and afterward decreases. At pH=5, the greatest removal of chromium was achieved. Biochar removal effectiveness for chromium was found to be 65 percent at pH=5 and lower at other pH levels. Similarly, a similar trend was seen in biomass. It has a chromium removal effectiveness of 47 percent at pH=2 and 58 percent at other pH values. For Chromium before pH 5, removal efficiency increased slowly, then, after 5 decreased. At low pH as compared to optimum pH, the cell surface sites were tightly linked to H+ ions, making other cations unavailable. However, there was an up rise in ligand with negative charges, resulting in increased cation binding with increased pH. The increase in pH value resulted in an increase in the negative charge surface of the batteries, which was advantageous to metal electrochemical adsorption. Based on the above findings, pH 5.0 was selected as the optimum value for chromium and used as the center point for subsequent experiments.

Conditions of the Experiment

Adsorbents = walnut shell as biomass and its biochar
Amount of Adsorbent = 0.05g

pH = 1-4

Concentration = 50ppm

Shaking time = 2 hours

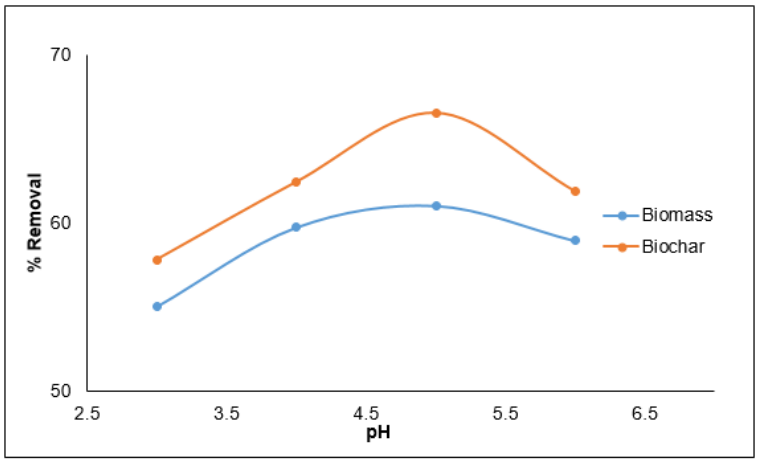

Fig. 7 Effect of pH

3.3 Effect of adsorbent dosage

Different adsorbents were utilized in this work to test the effectiveness of dosage rate on the removal of Chromium and lead metals, including walnut shell as biomass and its biochar. The working solution for chromium was kept at a pH of 5 with a starting concentration of 50 ppm. The experiment was carried out at dose rates of 0.05g, 0.1g, 0.15g, 0.2g, and 0.25g, with removal efficiency measured. The maximal uptake of chromium was measured at 0.25 g doses at their respective optimal pHs,

The experiment was carried out at a pH of 5 and a temperature of 20°C with an initial concentration of 1000 mg/L. The amount of the adsorbent was increased from 0.05 to 0.25 g. The effect of sludge-adsorbent dosage on copper ion removal efficacy and calcined sludge adsorption capacity was studied. It was discovered that as the adsorbent dose increased, so did the removal efficiency. This means that as the adsorbent dose increases, so do the available adsorption sites for Cr ions, resulting in higher removal efficiency.

According to the findings as to the increment of more active sites responsible for greater adsorption. Biochar made from walnut shells has removal effectiveness of 60 percent. Similarly, chromium removal efficiency was found to be 59 percent for the nano-sieved walnut shell, respectively. It shows the removal of chromium 75% (BM) < 78% (BC) at pH 5. The adsorbent dosage in the solution has a significant impact on metal adsorption. The results showed that cadmium removal efficiency increases as the amount of adsorbent increases from 0.25 g to 2 g, though there was no significant difference in adsorption at 1.75 and 2 g. This increase could be attributed to the adsorbent's overall increase in surface area, which doubled the amount of available active binding sites for adsorption.

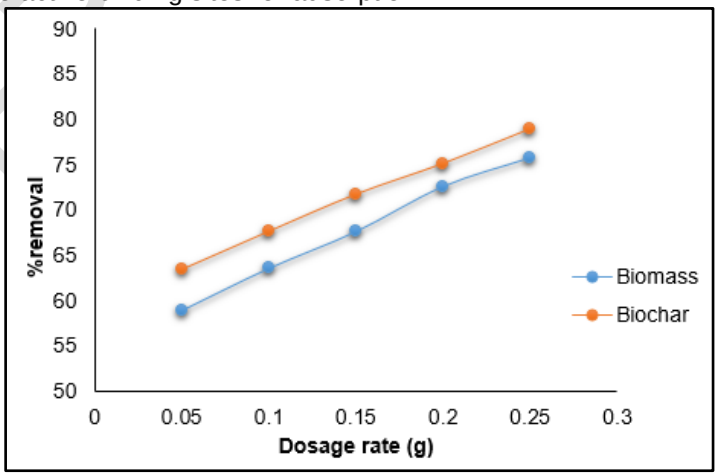

Fig. 8 Effect of Dose rate

3.4 Effect of Concentration

The initial concentration is crucial in overcoming the entire mass transfer and transporting particles between the aqueous and solid phases. In this work, the impact of a change in starting concentration on the removal of chromium was

investigated. Different adsorbents were used, including walnut shells as biomass and biochar. Different concentrations of 10ppm, 25ppm, 50ppm, 100ppm, 200ppm, and 400ppm solutions were generated at optimum pH of 5 for chromium with a 0.05 dose quantity. The highest chromium removal was recorded at 100ppm, with decreasing removal as concentration increased.

Maximum removal was reported by biochar and walnut shells at 100ppm concentrations, with biochar removing 61 percent and walnut shells removing 50 percent. The removal effectiveness reduces as the concentration rises or falls above or below 100ppm, as seen in the tables. Because this mechanism is dependent on active sites, there are fewer active sites for adsorbate molecules at greater concentrations. The findings revealed that as the concentration increases removal efficiency decreases. This was due to number of active sites which were greater for adsorbate molecules at lower concentration that binds the chromium molecules and result in fast adsorption. At highest concentration there was fewer number of active sites for adsorbate molecule as this process depends upon the availability of active sites of adsorbate.

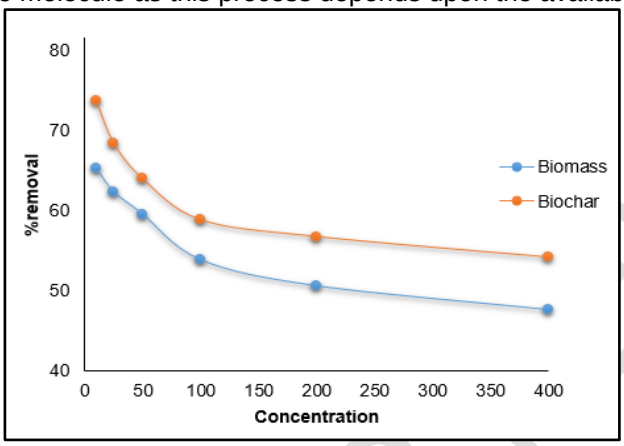

Fig. 9 Effect of Concentration

3.5 Effect of Contact Time

Adsorption rate increases as the contact between adsorbent and adsorbate increases. The surface of the walnut shell as biomass and biochar were all subjected to kinetic analysis. 0sec, 1,15, 30, 45, 60, 120, 240, 480, 600, 720, 1200, 1440 min were used to record the effect. The removal efficiency increases as the time interval grow until equilibrium is reached. As the time interval increases the removal capacity also increases until the equilibrium achieved. For chromium the removal efficiency increased as 63% (BM) <79% (BC) as the time increases from 0-1440 minutes.

Gradual increases were recorded up to 10 hours after equilibrium was reached and a straight line could be seen on the graph. At the optimum contact time, most materials were removed. The following trend was observed for chromium absorption capacity: Biochar > Biomass. The highest removal of chromium was 89 percent. A working solution with a concentration of 50ppm and 0.05g of certain adsorbents at their optimal pH has been created. The maximum removal time was 10 hours, and the removal was consistent for the next 24 hours.

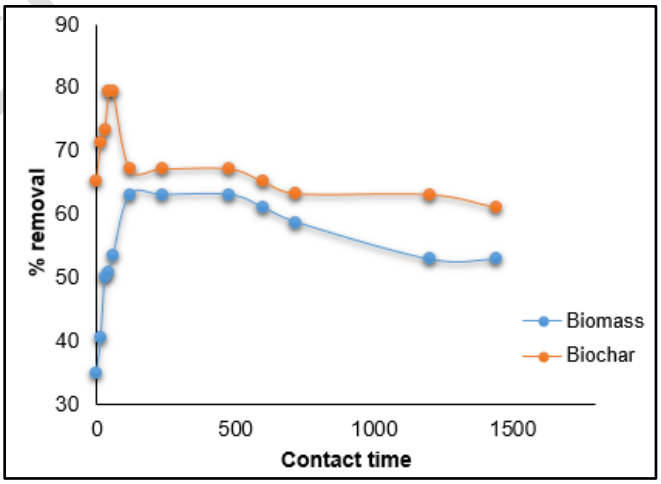

Fig. 10 Effect of Contact Time

4. KINETIC MODELS

The pseudo-first-order and pseudo-second-order kinetic models were applied to observed data to investigate the mechanism of chromium adsorption.

4.1 Pseudo 1St Order Kinetic Model

$$\ln(qe - qt) = \log qe - Kt/2.303 \qquad \text{Eq. 1}$$

Where qt mg/g is the quantity of sorption at time t and qe is the amount of sorption at the point of equilibrium and K1 (min-1) is the pseudo first order adsorption rate constant. The graphs of log (qe-qt) VS t were used to get the K1 and qe values. The rate is assumed to be proportional to the number of vacant sites in the model. The first order rate constant K1 and equilibrium adsorption capacity qe were determined using the slopes and intercepts of the plot of log qe-q VS t. The image makes it abundantly evident that the experimental adsorption capacity q Exp cannot be predicted by the pseudo first order equation.

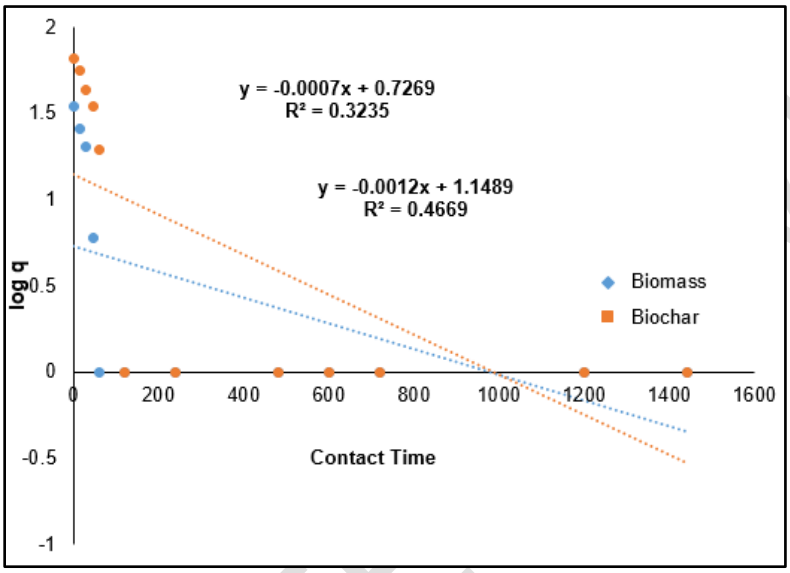

Fig. 11 Pseudo 1st order kinetic model for adsorption of Chromium

4.2 Pseudo 2nd Order Kinetic Model

$$t/qt = 1/K2q2 + 1/qet \qquad \text{Eq. (2)}$$

If pseudo-second order, K2 (mg/g) is the adsorption rate constant, and K2 and qe can be calculated from the intercept and slope of the t vs. qt plot. The pseudo-2nd order kinetics model was used to further evaluate the adsorption kinetics data. The adsorption is thought to be precisely proportional to the square of the number of vacant sites, according to the model. Walnut shell biomass and walnut shell biochar demonstrated Pseudo 2nd order kinetics follow-up with R^2 , values are given below in graph.

According to the study's findings, pseudo first order and second order rate equation kinetic formulations are candidates for providing an adequate explanation for the investigated adsorption systems. For the kinetic data of Chromium for adsorbents, the correlation coefficient R^2 obtained from the pseudo first order rate equation and the second order rate equation demonstrates that the second order rate equation is the best suited model. The vast majority of previous researchers developed a pseudo second order kinetic model to characterize the process of cation sorption on various adsorbents.The study of the velocity and mechanism of the surface process is called kinetics of adsorption. The kinetics study of adsorption process provides information and useful data on the feasibility of the removal of metals from water solutions on a larger scale. The data obtained from kinetic studies of removing lead and cadmium from aqueous solutions were fitted in a second-order kinetic model with an appropriate correlation coefficient of 0.99.

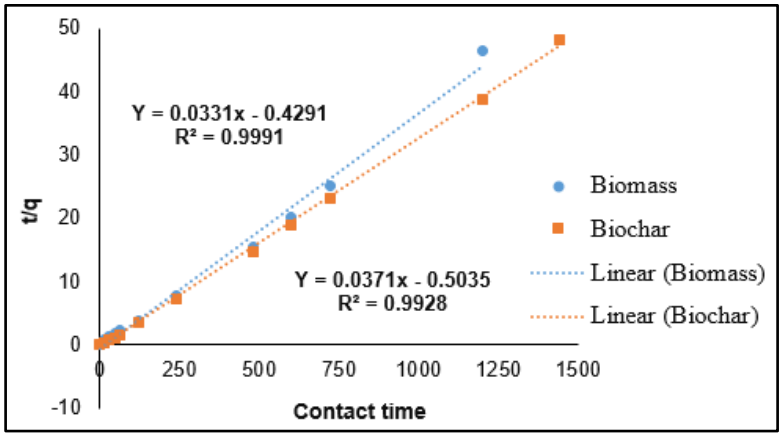

Fig. 12 Pseudo 2st order kinetic model for adsorption of Chromium

Table 1:Data for pseudo first and second order for adsorption of Chromium

Adsorbents	Pseudo first order model				Pseudo second order model		
	q_e (exp) (mg/g)	q_e (cal) (mg/g)	K_1 (min^{-1})	R^2	q_e (cal) (mg/g)	K_2 (g mg^{-1} min^{-1})	R^2
Biomass	30.9	5.33	-0.000303	0.32	26.95	0.0027	0.992
Biochar	38.9	14.08	-0.00052	0.46	30.21	0.0025	0.999

5. EQUILLIBRIUM MODELS

5.1 Langmuir Isotherm

$$\frac{Ce}{qe} = \frac{1}{KL \times qm} + \frac{Ce}{qm} \qquad \text{Eq. 3}$$

Where Ce is equilibrium heavy metal concentration in the aqueous phase ,qm is for complete monolayer adsorption capacity mg/g. Kl is Langmuir's constant. Adsorption is expected to occur at a particular homogeneous surface with an adsorbate. When the adsorbate particle covers a site, no further adsorption process talks place.

In more simplified terms, the statement of Langmuir is relied on the idea that adsorption will be at its highest level whenever a saturated solute monolayer already exists and there is no way for an adsorption molecule to go along the surface plane. So when an adsorbate molecule, such as copper or cadmium, occupies a site, it is reasonable to assume that no more adsorption may take place at that site. This is a presumption. A monolayer will be produced after equilibrium has been reached.

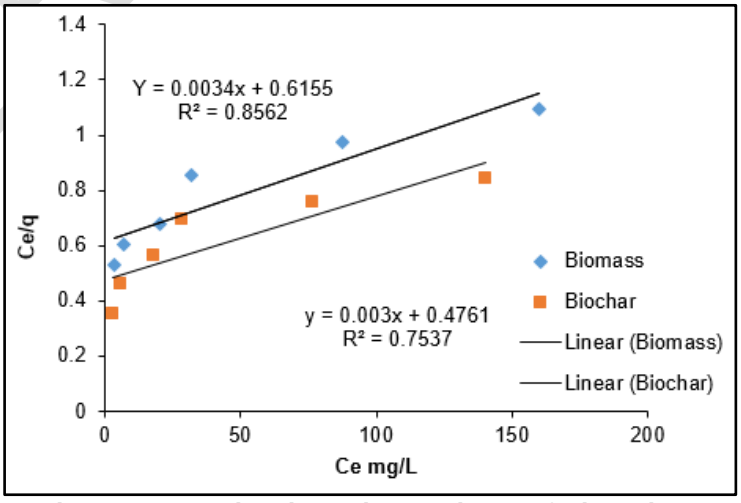

Fig. 13 Langmuir Adsorption Isotherm of Chromium

5.2 Freundlich isotherm

$$\ln(qe) = \frac{1}{n} LogCe + \ln(Kf) \qquad \text{Eq. 4}$$

The Freundlich isotherm is based on the sorption of a ligand on a heterogeneous surface of a sorbent.A value of 1/n below one or n. larger than one implies facile separation and advantageous multilayer adsorption of heavy metal ions from an aqueous media. Kf value denotes the adsorption capacity of the adsorbent. A better adsorption and the development of a substantially stronger connection between the heavy metal and adsorbent are indicated by the smaller value of 1/n that was achieved. In non-ideal sorption on a heterogeneous surface and multilayer sorption, Freundlich isotherm is used, which implies that the binding sites are not equal and/or independent.

The maximum R^2 is close to 0.99, and qexp is much closer to qe, indicating that the data followed the Freundlich isotherm and that adsorption occurs with multilayer formation rather than monolayer formation. Because it revealed a more linear behaviour than the Langmuir model owing to its better R2 values for both metals, the results suggested that the Freundlich model is appropriate for equilibrium modelling. This was determined by comparing the two models. The value of the correlation coefficient in the Freundlich model is quite close to one.
According tothe value of Regression correlation coefficient for Freundlich isotherm was found to be 0.99 suggesting Freundlich model as a better fit than the Langmuir model using functionalization of activated carbons with magnetic Iron oxide nanoparticles for removal of copper ions from aqueous solution from the waste water. The value of heterogeneity factor for Freundlich adsorption (*n*) was also in the range of favorable adsorption. Which clearly indicated the surface of adsorbent to be heterogeneous and the adsorption process to be multilayer suggesting that the concentration of the adsorbate molecules at equilibrium was directly related to the capacity of the adsorption.

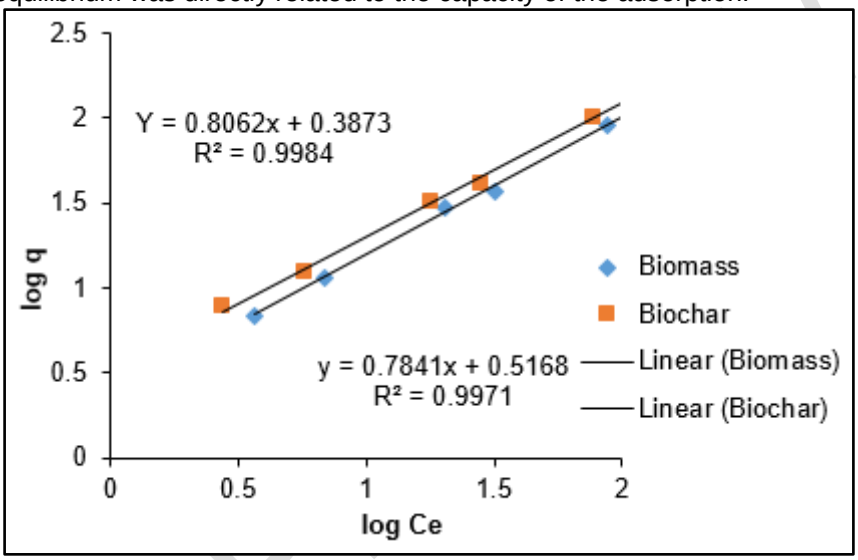

Fig. 14Freundlich Adsorption Isotherm of Chromium

Table. 2 Comparison of Equilibrium Models

Adsorbate	Adsorbents	Langmuir model				Freundlich model			
		q_e (exp) (mg/g)	q_e (cal) (mg/g)	K_L (L/mg)	R^2	q_e (cal) (mg/g)	1/n	K_F (mg/g)	R^2
Chromium	Biomass	146	294.11	0.0055	0.85	145.96	0.80	-0.94	0.99
	Biochar	166	333.33	0.0063	0.75	158.33	0.78	-0.66	0.99

6. COMPARISON OF ADSORBENTS

The solutions of 50ppm of chromium were prepared, shaken at 150rpm and 0.05g dose amount at optimum pH 5 were used to investigate adsorption efficiency. It was observed that walnut shell biochar has shown the maximum efficiency. Biochar is pyrogenic black carbon produced in an oxygen-limited environment by the thermal decomposition (e.g., pyrolysis) of carbon-rich biomass. Biochar has gained popularity in recent years due to its multifunctionality. When biochar-based agricultural waste materials were combined with nanoparticles, their functional activities increased.The impact of different adsorbents on the removal of chromium were as; Walnut shells biochar > Walnut shells biomass.

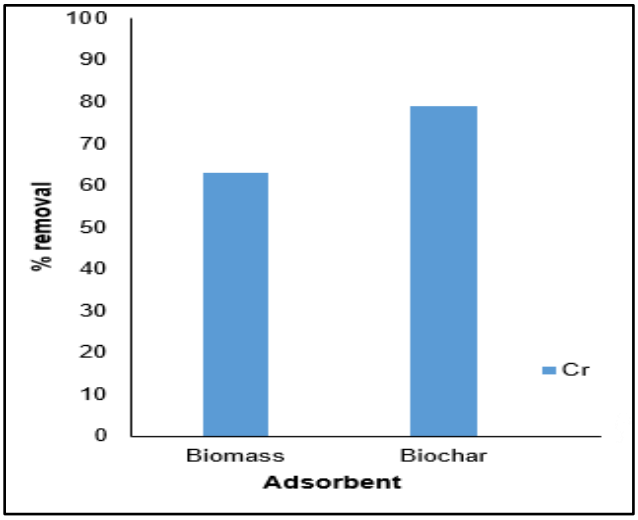

Fig. 15Adsorbents Efficiency

4. CONCLUSION

In this study, the effectiveness of walnut shell (WS) and walnut shell biochar (BC) for chromium (Cr) removal from wastewater using adsorption was compared. The effects of pH, biochar dosage, and contact time on Cr adsorption were investigated. The results showed that both WS and BC were effective adsorbents for Cr removal, with BC exhibiting a higher adsorption capacity and faster adsorption kinetics than WS. The maximum adsorption capacity of BC for Cr was 75.26 mg/g, which is significantly higher than the reported adsorption capacities of other low-cost adsorbents such as activated carbon and agricultural waste. The adsorption of Cr onto WS and BC followed pseudo-second-order kinetics, suggesting chemisorption as the rate-limiting step.The findings of this study suggest that BC is a promising adsorbent for Cr removal from wastewater. It is a sustainable and low-cost material that can be used to develop effective and efficient wastewater treatment systems. Further studies are needed to investigate the adsorption mechanism of Cr onto BC in more detail and to develop BC-based adsorbents with even higher adsorption capacities and faster adsorption kinetics.

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