(RESEARCH ARTICLE)

A study on the reduction of heavy metal ions (Cd^{2+} and Cr^{3+}) in waste water from chemistry laboratory by *Pericopsis elata* adsorbent

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Abstract

This research was aimed the at preparation and application of *Pericopsis elata* adsorbent in reducing the concentration of heavy metal ions present in waste water obtained from chemistry laboratory. Atomic Absorption Spectroscopy (AAS) was used to determine the concentration of heavy metal ions (Cd2+ and Cr3+) in laboratory waste water. The concentration of Cd and Cr were 155 and 122 mg/L. At a dosage of 0.25, 0.5 and 0.75 g the concentration ranged from 21.55 25.65 mg/L for Cr and 12.90 14.32 mg/L for Cd. At pH value of 2, 7 and 11, the concentration were 11.30, 20.33 and 39.50 mg/L for Cr and 15.30, 28.20 and 24.80 mg/L for Cd respectively. The concentration of Cr and Cd on adsorption increases with an increase in contact time of the adsorbate. At contact time of 20, 40 and 60, the adsorption concentration were 16.60, 19.30 and 29.40 (mg/L) for Cr and 10.50, 20.40, 48.10 (mg/L) for Cd. The results indicate that as the pH, contact time and temperature increases, the percentage removal of Cr and Cd also increases. As adsorbent dosage increased the percentage removal of Cr and Cd also increased. The result of the morphology showed a porous, rough and irregular surface with crystalline structure which indicated more macro pores for adsorption. It can be deduced that the *Pericopsis elata* adsorbent provides an external surface of porous and more reactive sites, which enhanced its adsorption capacity.

Keywords: Adsorbent; Reduction; Activated carbon; Waste Water; *Pericopsis elata*

1. Introduction

Africa Teak also known as Marsonia or Madrid, Afrormosia, nyinasa, asamela, assamela etc. The botanical name of the plant is *Pericopsis elata* (*P*. elata). It a medium to large tree that can grow up to 50 meters tall, found in relatively dry deciduous forests in West and Central Africa. The wood of *P. elata* is very valuable and durable timber that is often used in Africa. *P. elata* has been an important commercial timber species for over 60 years, and heavy exploitation of the tree has led to concerns about the species' ability to persist in the wild. The largest remaining stands of the tree are located in Cameroon, Congo-Brazzaville, Côte d'Ivoire, Democratic Republic of Congo, Ghana and Nigeria [1].

Activated carbon (AC) is perhaps one of the most widely used adsorbents for separation and recovery process in industry for environmental applications. Activated carbon (AC) is the non graphitizable carbon with a highly disordered microstructure. It is well known for high adsorption capacity due to its high surface area and porosity. Activated carbons are usually produced by either physical activation or chemical Activation process [2].

Carbon filtering is a method of filtrations that uses a bed of activated carbon to remove contaminants and impurities using chemical absorption. Each particle/granule of carbon provides a large surface area/pore structure, allowing contaminants the maximum possible exposure to the active sites within the filter media. Activated carbon works via a process called adsorption where pollutant molecules in the fluid to be treated are trapped inside the pore structure of

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the carbon substrate [3]. Carbon filtering is commonly used for water purification, air purifiers and industrial gas processing, for example the removal of siloxane sand hydrogen sulfide from biogas. It is also used in a number of other applications, including respirator masks, the purification of sugar cane and in the recovery of precious metals, especially gold. It is also used in cigarette filters [4]. Active charcoal carbon filters are most effective at removing chlorine, sediment, volatile organic compounds (VOCs), taste and odor from water [5]. The particle size will be used as part of the filter description. The efficacy of a carbon filter is also based upon the flow rate regulation when the water is allowed to flow through the filter at a slow rate, the contaminants are exposed to the filter media for a longer amount of time. Charcoal filters are used in a variety of fashions. The most common purpose for using a charcoal is to eliminate impurities. Gas masks are a good example of how charcoal filters provide protection to individuals by eliminating the impurities (chemical warfare, police riot squards etc). Charcoal filters are used in the purification process of many liquids (water processing facilities, coffee machines, aquariums, etc [6]. Any cheap material with a high carbon content, low in organic can be used as a raw material for the production of activated carbon. Acid base, oxidation reduction and specific adsorption characteristics are strongly dependent on the composition of the surface functional groups. The surface of conventional activated carbon is reactive, capable of oxidation by atmospheric oxygen and oxygen plasma steam, and also carbon dioxide and ozone [2]. This property is known as chemisorption. Many carbons preferentially adsorb small molecules. Iodine number is the most fundamental parameter used to characterize activated carbon performance. It is a measure of activity level higher number indicates higher degree of activation [7].

Metals ions are distributed throughout soil and sediment components and associated with them in various ways, including adsorption, ion exchange, precipitation and complexation and so on. Changes in environmental conditions, such as temperature, pH, redox potential and organic ligand concentrations can cause metals to be released from solid to liquid phase and sometimes cause contamination of surrounding waters in aquatic systems [8].

2. Material and methods

2.1. Sample Collection and Treatment

Pericopsis elata waste were collected randomly at six different locations within Wukari Local Government Area of Taraba State. The (carbon rich) raw materials wood was cut to 2 cm long manually with a knife. The pieces of the samples were washed with deionized water for the removal of adherent extraneous matter. The washed samples were dried in an oven at 105 °C for 17 hours to remove moisture. The sample was ground and kept in a drying cabinet for further analysis.

The production of activated carbon from *Pericopsis elata* waste was adopted from [9], the removal of red weight of each raw material was introduced into the furnace at 350 °C in the absence of air for one hour thirty minutes and to cool at room temperature.

2.1.1 Chemical Activation

The carbonated materials (carbon) from *Pericopsis elata* wood were crushed into powder using a crusher and sieved with a 1.88 mm sieve to obtain a uniform particle size. Measured weights of each carbonated materials were soaked in nitric acid of 0.1 M in a crucible. Each sample solution was stirred until the mixture turned to paste. The pastes were heated in a muffle furnace at 800 °C for 2 h in the absence of air to increase the surface area of the samples for adsorption purposes. The activated carbons were cooled to room temperature, washed with distilled water until their pH approximates 7 (no change in colour when tested with a red litmus paper) indicating no trace of nitric acid, dried for 3 h and stored in an air-tight nylon [9].

2.1.2 Treatment and Determination of Metal ion in Laboratory Waste Water

Method used by [10] was adopted with little modification volume of separation funnel. A 100 mL sample was adjusted to pH of 2.5 with 1M hydrochloric acid (HCl). A 2.5 mL of 1% ammonia pyrrolidine dithiocarbamate (APDC) and 10mL of methyl isobutyl ketone (MIBK) were added to the solution and shaken for 5 minutes in a separating funnel. The solution was allowed to stand to separate into two layers. The organic layer was emptied into a clean beaker, while the aqueous layer was returned to the separating funnel. A further 10 mL MIBK was to the aqueous layer and shake for another 5 minutes. The organic layer was emptied and combined with one previously collected. The process was repeated for all samples. The concentrations of Cd and Cr were then determined by AAS and the concentration of the metals in the sample were read from the calibration graph.

2.1.3   Stock Solution and Serial Dilution

The concentration of metal ions determined from the laboratory waste water were used as stock solution and several standard concentrations (10, 20, 30, 40 and 50 mg/L) were prepared from it by serial dilution using the equation:

$$C_1V_1 = C_2V_2 \text{ ....(i)}$$

Where:
C1 = concentration of stock solution.
C2= the desired concentration to be prepared.
V1= volume of stock solution taken
V2= volume factor to be diluted with.

2.2.   Determination of effect of initial solution of pH on adsorption

The effects of pH on the adsorption isotherms were studied using 0.25 g of sample added to 25 mL of 50 mg/L chromium, and cadmium solutions respectively. The pH were adjusted to five different pH of 2, 7, and 11 by drop wise addition of 0.1 M NaOH and 0.1 M HCl with the aid of a Hannah digital pH meter, it was then further contacted with 0.25 g of the adsorbent for 1hour with the aid of a mechanical shaker. It was then filtered and the residual chromium and cadmium was determined using AAS [11]

2.3.   Determination of effect of adsorbent dose on adsorption

The effect of adsorbent dose on adsorption was studied using 0.25, 0.5, and 0.75 g, portion of each asorbent to contact 25 mL each of 50 mg/L chromium, and cadmium respectively and stirred on a mechanical shaker for 1h, it was then fil tered and the residual phenol concentrations and cadmium conce-ntration determined AAS respectively [11].

2.4.   Determination of effect of adsorbent dose on adsorption

Solutions of chromium and cadmium were prepared at concentrations ranging from 10-30 mg/L respctively. 25 mL ea ch of the respective concentrations of Chromium and cadmium were contacted wit0.25 g of each of the adsorbents for 1 h. It was filtered and the residual and Cadmium concentration were determined using AAS [11].

2.5.   Determination of effect of contact time on adsorption

Separate 25 mL aliquots of 50 mg/L chromium and cadmium were contacted with 0.25 g of the adsoptions for 20, 40 a nd 60 minutes respectively in a mechanical shaker. After which each was filtered and the residual chromium and cad mium concentrations was determined using AAS [11].

2.6.   Determination of effect of temperature on adsorption

In the determination of the effect of temperature on adsorption, 25 mL each of 50 mg/L of chromium and cadmium were contacted with 0.25 g adsorbent at four different temperature of 28, 38 and 48 0C respectively in a thermostated water bath and stirred on a mechanical shaker for 1 h, it was then filtered and the residual chromium, lead and cadmium concentrations were determined using atomic absorption spectrophotometer (AAS).

2.7.   Adsorption Capacity and Efficiency

In all batch adsorption experiments, the amount of Chromium and Cadmium, Q_e (mg/g), was calculated by the mass ba lance equation adopted by [12].

$$Q_{e\ (mg/g)} = \frac{(C_o - C_e)}{M_a} v \text{...................} \text{(ii)}$$

where Qe represent the adsorption capacity, Co and Ce are the initial and residual Chromium and Cadmium concentrations (mg/L) respectively; V was the aliquot volume of chromium and cadmium solution (L) used and ma the mass of adsorbent in (g) used for a particular batch treatment. The percentage removal of chromium and cadmium was calculated as:

$$\% \ Removal = \frac{(C_o - C_e)}{C_o} \times 100 \text{...........(iii)}$$

% Removal is also called adsorption efficiency

3.   Results and discussion

Table 1 Concentrations of Metal Ions from Laboratory Waste Water Sample

Metals	Concentration (mg/L)
Cd	153
Cr	122

The results above showed the various concentration of metal ions (Cd^{2+}, Cr^{3+}) present in chemistry laboratory waste water. The high concentration of these metals may be due to the excessive use of Cadmium and Chromium salt for research and students practical.

Table 2 Effect of Adsorbent Dosage on Laboratory Waste Water Sample

Metals	Initial concentration (mg/l)	Adsorbent Dose 0.25 g	Adsorbent Dose 0.5 g	Adsorbent Dose 0.75 g
Cr (mg/l)	50	21.55	25.65	29.29
Cd (mg/l)	50	12.90	13.60	14.32

The concentration of Cr and Cd on adsorption decreases with increase in dosage of the adsorbent. At dosage of 0.25, 0.5 and 0.75 g the concentration ranged from 21.55 - 29.29 mg/l for Cr and 12.90 - 14.32 mg/l for Cd respectively. This is evident that there is a wide decrease in the concentration of Cd than Cr which means Cd ions was adsorbed more than Cr as the dose increases.

Table 3 Effect of pH on Laboratory Waste Water Sample

Metals	Initial concentration (mg/l)	pH		
		2	7	11
Cr (mg/l)	50	11.30	20.33	39.50
Cd (mg/l)	50	15.30	24.80	28.20

The removal of metal ions from wastewater demonstrated by adsorption is interrelated to the pH of the sample, as it affects the surface charge of adsorbents, the degree of ionization, and the species of adsorbate. The pH of the aqueous solution is a significant tool controlling adsorption process and thus the role of H+ concentration was observed from the adsorbent at varied pH of 2 - 11 (Table 3). As the solution pH increases, the onset of the metal hydrolysis and the precipitation began at pH > 7 and the onset of adsorption therefore occurs before the beginning of hydrolysis [13]. The concentration of Cr and Cd on adsorption increases with increase in pH. At pH of 2, 7 and 11, the concentrate on ranges from 11.30, 20.33 and 39.50 mg/L for Cr and 15.30, 24.80 and 28.20 mg/L for Cd respectively. Cd showed high level of adsorption as the increases compared to Cr.

Table 4 Effect of Initial Adsorbate Concentration on Laboratory Waste Water Sample

Metals	Sample weight (g))	Initial Concentration (mg/l)		
		10	20	30
Cr (mg/l)	0.25	9.52	12.54	15.59
Cd (mg/l)	0.25	8.56	11.60	16.60

The concentration of Cr and Cd on adsorption increases with increase in concentration of the adsorbate. Serial increase in concentration of Cr at 10, 20 and 30 mg/L, increases from 9.52, 12.54 and 15.59 mg/L and also the concentration of Cd also increases from 8.56, 11.60 and 16.60 mg/L. It is obvious that for higher initial concentration, more efficient

utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient [14] and due to utilization of active sites is larger surface area [15].

Table 5 Effect of Contact Time on Laboratory Waste Water Sample

Metals	Initial Concentration (mg/l)	Time (Min)		
		20	40	60
Cr (mg/l)	50	16.60	19.30	29.40
Cd (mg/l)	50	10.50	20.40	48.10

The concentration of Cr and Cd on adsorption increases with increase in contact time of the adsorbate. At contact time of 20, 40 and 60 the adsorption concentration ranges from 16.60, 19.30 and 29.40 (mg/L) for Cr and 10.50, 20.40 and 48.10 for Cd.

Table 6 Effect of Temperature on Laboratory Waste Water Sample

Metals	Initial Concentration (mg/l)	Temperature (^{0}C)		
		28	38	48
Cr (mg/l)	50	19.60	20.10	32.60
Cd (mg/l)	50	15.65	26.95	40.85

The concentration of Cr and Cd on adsorption increases with increased in temperature of waste water. At temperature 28, 38 and 48 the concentration increased from 19.60, 20.10 and 32.60 mg/L for Cr and 15.65, 26.95 and 40.85 for Cd. However, Cr showed high level of adsorption. Similar results was recorded by [16] and observed that Temperature increase had a positive effect on the uptake of Cd (II) and Cr (VI) ions onto all adsorbents.

Table 7 Data for adsorption capacity and efficiency (percentage removal) of Cr and Cd on the adsorbent at Different pH

Metals	pH	C_0 mg/L	C_e mg/L	Q_e (mg/g)	% Removal
Cr	2	25	11.30	1050	21.00
	7	25	20.33	2967	59.34
	11	25	39.50	3870	77.40
Cd	2	50	15.30	2180	43.60
	7	50	28.20	2520	50.40
	11	50	24.80	3470	69.40

The adsorption capacity of Chromium at different pH 2, 7 and 11 increase with increase in pH from 1050, 2967 and 3870 mg/g while for Cd 2180 3470 mg/g. As the pH increases, the percentage removal of metal ions increases. Cr removal ranged from 21.00 77.40 % and Cd from 43.60 69.40%. It was observed [14] that increase in adsorption as pH of Cd2+ solution increases, at pH of 5.0, adsorption of Cd2+ on SPP-kaolinite clay was 55.12% which is similarly to the findings of this research at pH of 11. [17] showed that Percentage removal of heavy metals Cr(III) and Cd(II) increases with increasing in pH value as optimum adsorption occurred at pH=12 while pH of 11 was observed in this work.

Table 8 Data for adsorption capacity and efficiency (percentage removal) of Cr and Cd at different adsorbent Dosages on the Adsorbent.

Metals	Dosage	C_0 mg/L	C_e mg/L	Q_e (mg/g)	% Removal
Cr	0.5	50	21.55	1218	41.42
	0.25	50	25.65	2737	48.70
	0.75	50	29.29	2845	56.90
Cd	0.25	50	12.90	1189	71.36
	0.50	50	13.60	1820	72.80
	0.75	50	14.32	3710	74.20

The adsorption capacity of Chromium and cadmium at different dosage 0.5, 0.25 and 0.75 (g) increase in adsorption capacity from 1218 2845 mg/g for Cr and 1189 3710 for Cd mg/g respectively and an increase in percentage removal range from 41.42 - 56.90 for Cr and 71.36 - 74.20 for Cd. In this case Cd showed high level of adsorption. A dosage of 0.5 g could remove 41.41 % of Cr and 71.36 % of Cd content of the wastewater. On the whole, the effect of absorbent dose on the percent removal of Cr and Cd, at concentration of 50 mgL-1 indicates that increasing the absorbent dose for both adsorbents, percent removal increment up to 56.90 and 74.20 % was observed at a dosage of 0.75 g.

Table 9 Data for adsorption capacity and efficiency (percentage removal) of Cr and Cd on the adsorbent at Different Contact Time on the Adsorbent

Metals	Time (Min)	C_0 mg/L	C_e mg/L	Q_e (mg/g)	% Removal
Cr	20	50	16.60	2060	41.20
	40	50	19.30	3070	61.40
	60	50	29.40	3340	66.80
Cd	20	50	10.50	1900	33.60
	40	50	20.40	2960	59.20
	60	50	48.10	3950	79.00

The adsorption capacity of Chromium and cadmium at different contact time 10, 40 and 60 minutes recorded an increase in adsorption capacity from 2060 - 3340 and 1900 - 3950 mg/g. The Percentage removal of Cr ranged from 41.20 - 66.80 and Cd from 33.60 - 79.00 %. The result showed that maximum removal of Cr and Cd was achieved at 60 minutes while minimum removal was at 20 minutes respectively. The Cr and Cd adsorption takes place at the more reactive sites. As these sites are increasingly occupied, the more challenging the sorption becomes; and the sorption process tends to be more unfavorable. This is the overall distinctive of adsorption of this type of metal ion [18]. These variations and changes in metal ion uptake rate could be due to two different adsorption processes, namely a fast ion exchange followed by chemisorptions [19]. A sharp increase in removal rate was however noticed on the removal of Cr and Cd ions from the wastewater by the adsorbent as a function of time.

It was observed by [20] that the percentage of cadmium adsorption increased with increasing shaken due to sufficient contact between the metal ions in solution and the adsorbents binding sites that promotes effective transfer of cadmium ions to the adsorbents sites. The results of Cr (III) and Cd (II) reduction using activated coconut leaf powder reported by [21] showed higher percentage removal of Cr and Cd (87 and 85 %) than those obtained in this study. This increase maybe due to the activation of adsorption site takes place leading to increased adsorption probably through surface exchange mechanism [22].

Table 10 Data for adsorption capacity and efficiency (percentage removal) of Cr and Cd on the adsorbent at Different Temperature on the Adsorbent

Absorbate	Temp (°C)	C_0 mg/L	C_e mg/L	Q_e (mg/g)	% Removal
Cr	28	50	19.60	1740	34.80
	38	50	20.10	2990	59.80
	48	50	32.60	3040	60.80
Cd	28	50	15.65	3435	18.30
	38	50	26.95	2305	46.10
	48	50	40.85	915	68.70

The adsorption capacity of Chromium at different temperatures 28, 38 and 48 (°C) increase with increase in temperature from 1740, 2990 and 3040 mg/g and increase in percentage removal at the same temperature from 34.80 60.80 %. Similar result was observed in Cr with an increase in adsorption capacity 915 - 3435 mg/g with increase in percentage removal l18.30, 68.70 % at the same temperature for Cd. Similar results was reported by [14] whereby an increase in temperature from 25 to 45 °C, the adsorption capacity increased for Cd^{2+} from 10.37 to 13.25 mg/g. This indicates that the adsorption reaction was endothermic in nature.

Table 11 Data for adsorption capacity and efficiency (percentage removal) of Cr and Cd on the adsorbent at Initial Concentration on the Adsorbent

Absorbate	Mass ($_g$)	C_0 (mg/L)	C_e (mg/L)	Q_e (mg /g)	% Removal
Cr	0.25	10	9.52	48.00	37.30
	0.25	20	12.54	1441	48.03
	0.25	30	15.59	7450	64.80
Cd	0.25	10	8.56	1340	14.40
	0.25	20	11.60	1440	42.00
	0.25	30	16.60	8400	44.70

The adsorption capacity of Chromium and cadmium at different concentration 10, 20 and 40 (mg/) increase in adsorption capacity 1441 - 7450 and 1340 - 8400 mg/g with increase in percentage removal of 37.30 - 64.80 (%) for Cr and14.40 - 44.70 for Cd.

The effect of Cr and Cd ions concentration on the sorption by the adsorbent was investigated by varying the metal concentration from 10 to 30 mg/l at a pH of 2.0 for 20 minutes. It was observed that the percent metal ions removal of the adsorbent increased with increasing metal ions concentration. It is obvious that for higher initial concentration, more proficient utilization of sorption sites is expected owing to a greater driving force by a higher concentration values.

3.1. SEM Analysis

SEM: AZeiss EVO 50 Scanning Electron Microscope (SEM) was used in this study.

The structure of the raw material marsonia wood waste was observed at magnification of 10 - 100,0
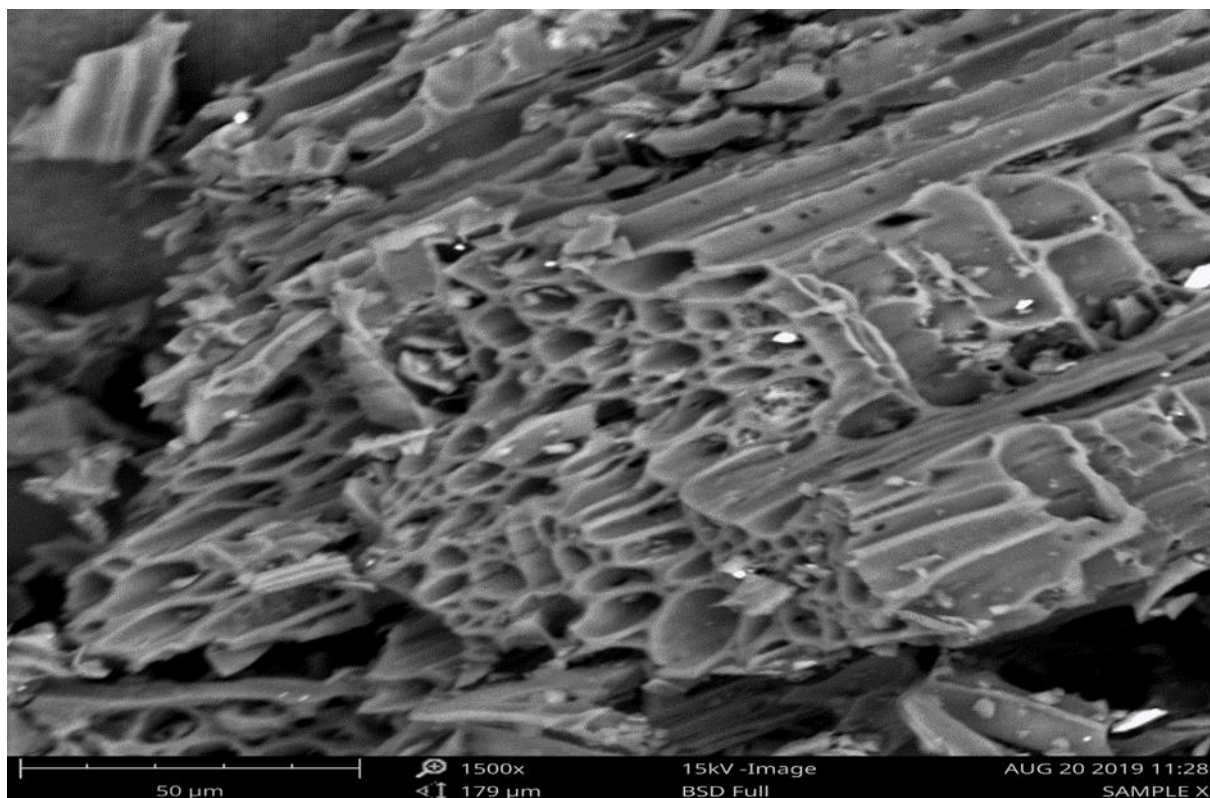
Figure 1 SEM Porosity

The SEM micrographs indicated macro pores in the *Pericopsis elata* adsorbent with large cavity. Also, the SEM results showed the surface morphology feature of the adsorbents which is an indication that important interaction can occur between the metal ions and adsorbent granule interface in the experimental conditions [1]. The plate shown above showed a porous, rough and irregular surface with crystalline structure which indicated more macro pores for adsorption. Similar observation was reported by [23]. It can be concluded that the *Pericopsis elata* adsorbent provides an external surface of porous and more reactive sites which enhanced its adsorption capacity.

4. Conclusion

The results showed that the concentration of Cr and Cd on adsorption decreased with increased in dosage of the adsorbent. The pH of synthetic waste water increased with an increased in the concentration of Cr and Cd on adsorption. The results also indicated that as the pH, contact time and temperature of the synthetic waste water increased, the percentage removal of Cr and Cd also increased. The results showed evidence for the removal of Cr and Cd heavy metals ions by *Pericopsis elata*.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declared no conflict of interest.

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