Int. J. Adv. Res. Biol. Sci. (2024). 11(10): 1-10

International Journal of Advanced Research in Biological Sciences
ISSN: 2348-8069
www.ijarbs.com
(A Peer Reviewed, Referred, Indexed and Open Access Journal)
DOI: 10.22192/ijarbs Coden: IJARQG (USA) Volume 11, Issue 10-2024

Research Article

DOI: http://dx.doi.org/10.22192/ijarbs.2024.11.10.001

Application of Orange fruit peels for the adsorption of heavy metal concentrations in Asariver.

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Abstract

Heavy metal pollution affects all living things and can be removed or reduced using a range of standard or conventional techniques which are more expensive. The method of using organic wastes of an effective, affordable, and novel solution for the adsorption process is more preferable. Orange peel was employed for adsorption of heavy metals from a contaminated water sample and its descriptive evaluation was performed using Fourier Transform Infrared (FTIR), Scanning Electron Microscope (SEM) coupled with Energy dispersive X-ray (EDX). An initial evaluation of heavy metals in the samples was carried out using Atomic Absorption Spectrophotometer. A batch experiment was set up to adsorb the heavy metals from the samples of water at three different concentrations (0.5g, 0.10g and 0.15g) for a total retention time of 72 hours (24, 48, and 72h). Five heavy metals were evaluated from the samples and these are: Cadmium(0.022mg/l), Zinc(2.852mg/l), Iron(35.660mg/l), Chromium(0.084mg/l) and copper(0.062mg/l). The orange peel biomass had a maximum metal adsorption efficiency (100%) for both Cadmium(0.00) and Chromium(0.00) while removal efficiency for other metals was between A and B%. The outcome of the research has presented orange peel as a potential adsorbent for the removal of heavy metals from contaminated samples.

Keywords: Orange peels, Heavy metals, Adsorption, FTIR, SEM, EDX, Adsorbate dosage and Time.

1. Introduction

Heavy metal removal from wastewater before discharge into running waters or rivers is a major concern since heavy metals pose substantial environmental risks (Marin *et al.,* 2010).Due to their inability to biodegrade, these chemicals are stable and enduring environmental pollutants as reported by Sud*et al.,* 2008.When industrial inorganic effluents are dumped into rivers and dams, they tend to accumulate toxic metal ions in the food chain. Hazardous heavy metal ions can be ingested by living beings due to their high solubility in aquatic environments. Once heavy metals enter the food chain, they may accumulate to large concentrations in the human body. Some pollutants, such as lead (Pb), chromium (Cr), cadmium (Cd), oils and grease etc., are extremely poisonous and harmful even in very small amounts, such as ppb (parts per billion range) as reported by Verma and Dewivedi, 2013. If ingested in greater amounts than accepted, the metal ions can cause serious health problems (Dadhaniya *et al*., 2009).Even with very low concentrations, heavy metal ion pollution in water causes ecological problems, according to Essawy *et al*. (2004), which increased the demand for materials that can bind these metal ions efficiently and the major issue in the realm of water purification is the removal of these heavy metal ions.

Innovations for removing heavy metals include ion exchange, electrodialysis chemical oxidation/reduction, ultra filtration, precipitation, reverse osmosis, and solvent extraction, but these processes have drawbacks, including high costs, the need to dispose of leftover metal sludge, and the inadequacy of small-scale industries as reported by Manish *et al*.,2015 and Guo *et al*., 2011. The adsorption process has drawn interest and evolved into a substitute for other traditional methods because the materials are nonhazardous, naturally occurring, and inexpensive, biodegradable in nature which are increasingly being used nowadays to remove heavy metals from wastewater before being discharging to the rivers.

Orange peel is typically discovered as waste and is handled accordingly. It has numerous functional groups, including carboxyl and hydroxyl, which make it a suitable adsorbent for removing heavy metal ions as reported by Annadurai *et al*., 2003,Guo*etal*., 2011 and Ekpete *et al*., 2010. Because of its primary components, pectin, cellulose, lignin and hemicellulose which include functional groups as potential metal location for binding, it also has a lot of promise for use as a biosorbent material (Kaushik *et al*., 2009). According to Acar *et al*. 2015,Abid *et al*., 2016 and Tran *et al*., 2016, orange peel is a desirable and affordable alternative for removing metal ions from waste water.

This study aimed to assess the efficient capacity of the peels from orange in adsorbing various heavy metal ions (Pb, Cr, Cd, Cu, Fe, and Zn) from the Asa River. It also investigated on how contact time and the initial concentration of metal ions affected the biosorption efficiency.

2. Materials and Methods

Water Sample Collection

Water samples were obtained from the Asa River at three distinct locations along the river. The Asa River is a shallow river with a depth of less than 10 meters from the surface. The locations were chosen according to how easy it was to access the river and what kinds of activities were available along the river at those locations. The upper, middle, and lower streams were the three points that were collected. Upper Stream Point was utilized as a control because of its very low levels of human activity, while middle stream point has wastewater released directly to the river from a pharmaceutical factory and the lower stream point receives a lot of highway runoff water as well as effluent discharged from the steel and wire fabrication industry.

Orange Peel collection and preparation

Orange fruits was collected from Ogbomosho town in Oyo State as shown in plate 1. The outer skin of the orange fruit was first peeled off in order to obtain the orange peel. The peel was then washed with ordinary water from the tap to eliminate any potential foreign objects (dirt and sands) that may have been present. To reduce the size as shown on the plate 2, washed sample material was dried at 1000C in an electrical oven for a whole night and then crushed using a mortar and pestle. After being carbonized for 15 minutes at 400°C, 250 g of the tiny fragments were activated for two to three hours at 500 oC using 1.0 M $ZnCl_2$. The activated materials were taken out of the furnace and allowed to naturally cool to room temperature in preparation for the adsorption process. After being crushed to a geometric mean particle size of 180–150 µm, orange peel activated carbon was kept at room temperature according to Mohamed and Amaal, 2017.

Plate 1: The plate showing orange peels.

Plate 2: The plate showing grinded and dried orange peels.

Adsorption process on Orange Peels

Lead, chromium, zinc, copper, and cadmium were all prepared as separate serial standard solutions from stock solutions (1000 mg/L) of each metal. Analyzing the adsorption of different metals on orange peel carbon adsorbent was done in batches. In a 250 ml flask, the activated carbon was first added, and then 20 ml of a common heavy metal solution. The mixtures were centrifuged for five minutes at 5000 rpm after being continuously agitated for two hours. Each sample's supernatant was then examined using an Atomic Spectrophotometer) according to Horsfall *et al*., 2006 and Zulkaliet al., 2006.

Using an energy dispersive X-ray (EDX) analyzer and a JEOL JSM-6390 model scanning electron microscope, SEM analysis was done on the orange peel carbon samples to examine their elemental composition and surface morphology. Because SEM has outstanding clarity, higher magnification for closely spaced materials is achievable. According to Bello *et al*., 2017, Mohamed and Amaal, 2017 andOlakunle *et al*., 2017, Using a spectrometer (Thermo Nicolet, NEXUS, USA) at ambient temperature, the carbonaceous components of the adsorbates were characterized by diffuse Fourier-transform infrared analysis (FTIR) to qualitatively determine the functional groups in frequency ranging between 4000 to 400 cm-1.

Statistical Analysis

Statistical analysis was performed on the data using SPSS (Statistical Packaging for Social Sciences) version 22.0. The one-way analysis of variance (ANOVA) and the Duncan multiple range test were used to the data. The significance level is set at $p \leq 0.05$.

3. Results and Discussion

Evaluation of Functional Groups on orange peels
An FT-IR spectrophotometer was also used to identify the functional groups on the orange peels, and the spectra showed five distinct strong peaks at 3407.00, 2925.30, 1602.00, 1377.00, and 1029.00 as shown in figure 1.

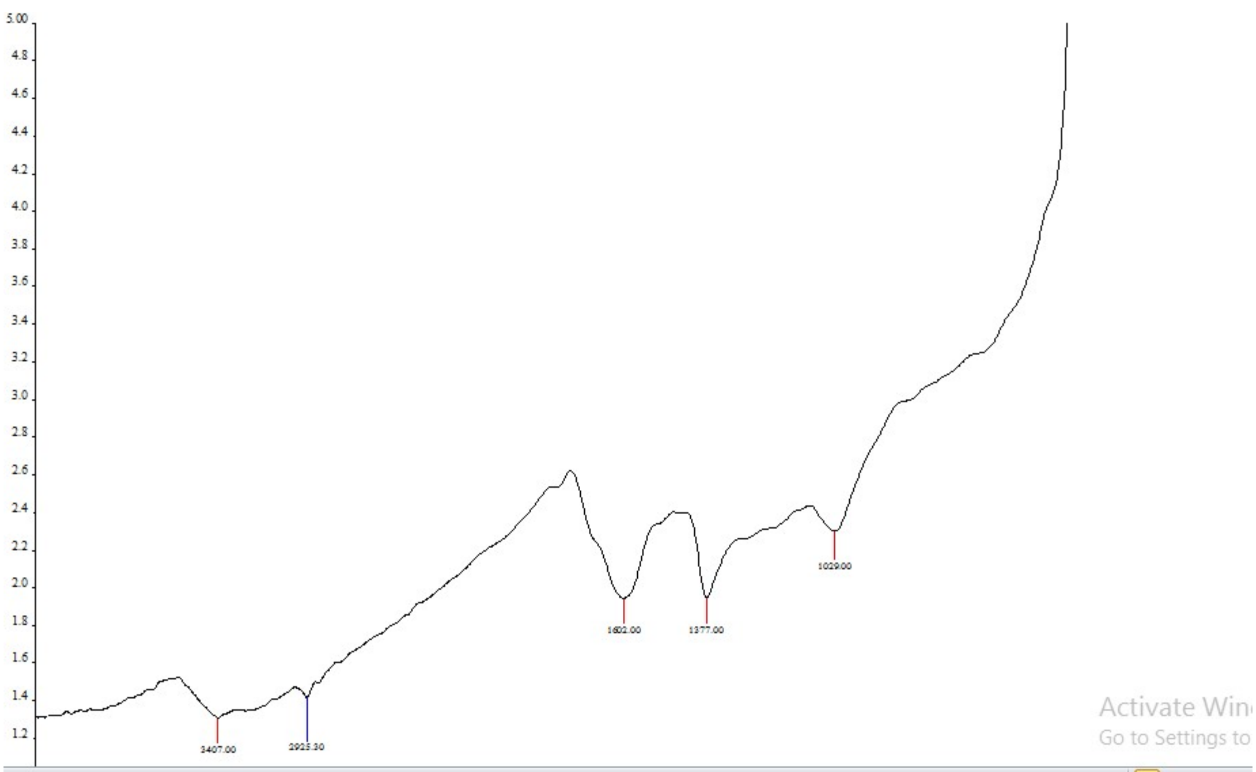

Figure 1: FT-IR result of Orange Peels
Characterization of orange peels

Orange peels were subjected to scanning electron microscopy, which showed the different large pore of the adsorbent as shown in plate 3 and plate 4 while the elemental composition was revealed with energy dispersive X-ray which shows the presence of eight elements (O, Zn, Fe, Si, Ca, K, S, Ag). Oxygen is revealed to be the highest element having elemental weight of 40.20% and the activated orange peels as shown in figure 2 and figure 3.

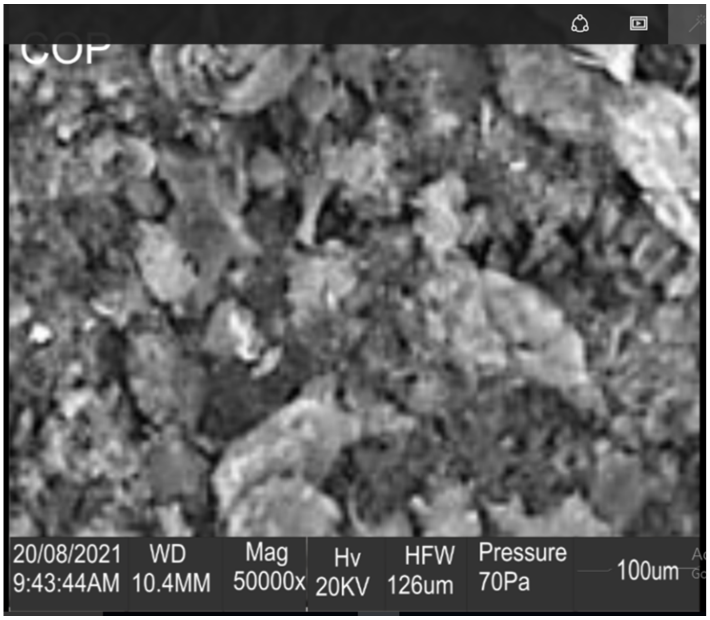

Plate 3: SEM of carbonized orange peels

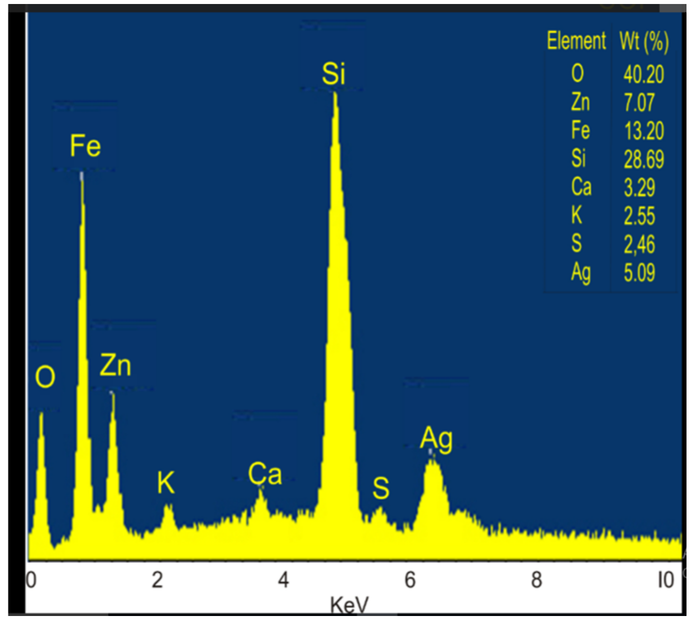

Figure 2: EDX of carbonized orange peels

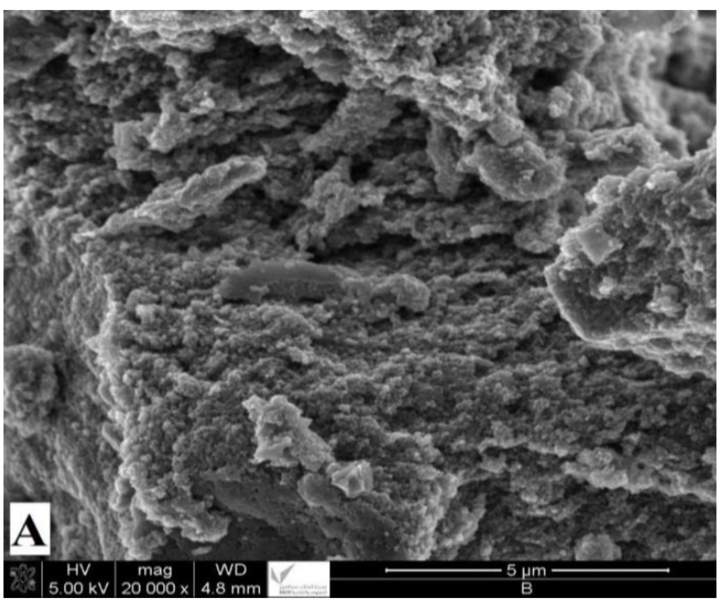

Plate 4: SEM of Activated orange peels

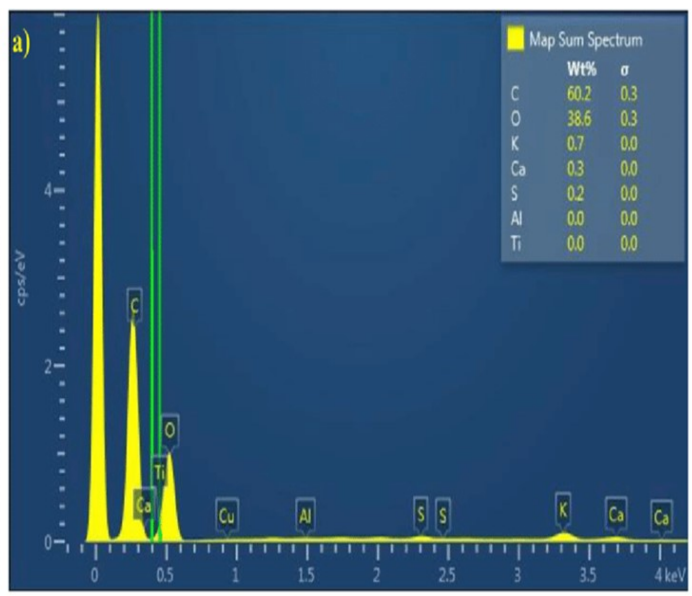

Figure 3 : EDX of Activated orange peels

Adsorption Efficiency of Carbonized Orange peel (COP) and activated carbonized orange peels(ACOP) in the Removal of Heavy Metals .

Carbonized orange peel was also used as one of the bioabsorbent in removing heavy metal ions from water samples with different contact times (24, 48, and 72 hours) and concentrations (0.5, 10, and 15 grams). Activated carbonized orange peels was used for the removal of particles of heavy metals, and it was discovered that the heavy metal ions of chromium and cadmium were totally removed in all the concentrations and varying time intervals as shown in Table I and Table IIwhile copper, Zinc and iron exhibits the greatest adsorption capacities of reducing the metal ions to a minimal level at varying concentrations and contact times intervals as shown in Table III, IV and V respectively.

The water samples from LS was reduced to a lower concentration of copper. After the LS water sample was treated with the COP bio-sorbent, the amount of copper in the sample decreased from 0.015mg/l to 0.000mg/l at 0.15g during 72hrs and ACOP from 0.015mg/l to 0.001mg/l at 0.15g during 72hrs.For LS, there was no noticeable reduction in the metal ion's starting concentration at 0.10g and 0.15g at 48 hrs, US at 0.10g and 0.15g at 48hrs with the absorbent of COP at 0.001mg/l and at 0.10g and 0.15g at of the bio-sorbent of ACOP at 48hrs 0.020 and 0.010 at 72 hrs at 0.10g and 0.15g in US respectively. This can be the consequence of the sample's original low concentration of copper metal ions. The metal was effectively reduced in all samples by the 0.15g bio-sorbent dosage at different contact times. as previously reported by Khalfaoui and Meniai, 2012

Based on the results, it was possible to determine that the best contact time for removing copper from all of the samples was 72 hours, and the best dosage of biosorbent for reducing copper was 0.15 grams. Zinc was removed from the collected samples with the maximum adsorption efficiency (sample MS), reducing the concentration from 1.172 mg/l to 0.422 mg/l with 0.15 g of the bio-sorbent after 72 hours.

Table I:Iron concentration in the water samples treated with carbonized and activated carbonized orange peels.

	COP			ACOP			STD
IRON (Fe)	LS	MS	US	LS	MS	US	WHO
Initial conc. (mg/l)	35.660	10.764	2.001	35.660	10.764	2.001	0.300
0.5g (24hrs)	6.833	5.091	1.571	4.373	7.765	0.993	
0.10g (24hrs)	4.753	3.650	1.094	3.523	6.443	0.834	
0.15g(24hrs)	3.423	3.043	1.035	2.673	4.093	0.634	
0.5g (48hrs)	2.610	3.101	0.974	1.092	4.003	0.584	
0.10g(48hrs)	1.580	2.563	0.809	1.120	3.081	0.511	
0.15g (48hrs)	1.430	1.762	0.702	0.853	2.045	0.429	
0.5g (72hrs)	1.142	1.108	0.638	0.752	1.560	0.300	
0.10g (72hrs)	1.045	1.082	0.448	0.656	0.975	0.361	
0.15g (72hrs)	1.023	1.002	0.320	0.532	0.910	0.320	

Table II :Copper concentration in the water samples treated with carbonized orange peels and activated carbonized orange peels.

	COP			ACOP			STD
Copper (Cu)	LS	MS	US	LS	MS	US	WHO
Initial conc. (mg/l)	0.015	0.062	0.057	0.015	0.062	0.057	1.000
0.5g (24hrs)	0.015	0.060	0.052	0.010	0.050	0.042	
0.10g (24hrs)	0.002	0.057	0.050	0.010	0.047	0.031	
0.15g(24hrs)	0.001	0.050	0.050	0.009	0.034	0.030	
0.5g (48hrs)	0.001	0.050	0.049	0.008	0.030	0.028	
0.10g(48hrs)	0.001	0.042	0.048	0.065	0.030	0.020	
0.15g (48hrs)	0.001	0.032	0.048	0.060	0.022	0.020	
0.5g (72hrs)	0.000	0.020	0.035	0.060	0.020	0.016	
0.10g (72hrs)	0.000	0.022	0.000	0.051	0.019	0.010	
0.15g (72hrs)	0.000	0.000	0.000	0.001	0.003	0.010	

Table III: Zinc concentration in the water samples treated with carbonized orange peels and activated carbonized orange peels.

	COP			ACOP			STD
Zinc (Zn)	LS	MS	US	LS	MS	US	WHO
Initial conc. (mg/l)	2.852	1.172	2.123	2.852	1.172	2.123	3.00
0.5g (24hrs)	2.387	1.018	2.000	2.102	1.026	1.743	
0.10g (24hrs)	1.864	1.000	1.929	1.849	1.010	1.420	
0.15g(24hrs)	1.642	0.957	1.800	1.673	0.862	1.210	
0.5g (48hrs)	1.501	0.911	1.760	1.360	0.721	1.100	
0.10g(48hrs)	1.370	0.832	1.631	1.248	0.529	0.723	
0.15g (48hrs)	1.042	0.714	1.103	1.220	0.391	0.652	
0.5g (72hrs)	0.921	0.700	0.843	1.124	0.227	0.501	
0.10g (72hrs)	0.854	0.632	0.741	1.103	0.247	0.207	
0.15g (72hrs)	0.795	0.422	0.459	0.736	0.093	0.085	

Table IV:Chromium concentration in the water samples treated with carbonized orange peels and activated carbonized orange peels.

	COP			ACOP			STD
Chromium (Cr)	LS	MS	US	LS	MS	US	WHO
Initial conc. (mg/l)	0.084	0.278	0.240	0.084	0.278	0.240	0.050
0.5g (24hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.10g (24hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g(24hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.5g (48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.10g(48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g (48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.5g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.10g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	

Table V: Cadmium concentration in the water samples treated with carbonized orange peels and activated carbonized orange peels.

	COP			ACOP			STD
Cadmium (Cd)	LS	MS	US	LS	MS	US	WHO
Initial conc. (mg/l)	0.020	0.022	0.021	0.020	0.022	0.021	0.003
0.5g (24hrs)	0.000	0.000	0.000	0.00	0.0000.000		
0.10g (24hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g(24hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.5g (48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.10g(48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g (48hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.5g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.10g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	
0.15g (72hrs)	0.000	0.000	0.000	0.000	0.000	0.000	

Both carbonized and activated carbonized orange peels were efficient for the removal of chromium metal ions in Asa river, in all the water samples of US, MS and LS at different contact time (24hrs, 48hrs, 72hrs) and bio-sorbent dose (0.5g, 0.10g, 0.15g),The bio-sorbent made it possible for the chromium metal ions to be fully adsorbed, which made removal easier as reported by Ekpete *et al*., 2010 and Dadhanya *et al*., 2009.

In all samples that were collected, the orange peels were effective in removing cadmium metal ions. The removal of cadmium metal ions was made easier by the bio-sorbent's ability to totally adsorb the metal ions at different contact times (24, 48, and 72 hours) and doses (0.5, 0.10, and 0.15 grams). The results of Priyanka Kumari's 2017 study and Guo *et al*.'s 2011 study, which demonstrated orange peels' effectiveness in adsorbing heavy metal ions, concur with this investigation.

4. Conclusion

Because orange peels contain cellulose,pectin, hemicellulose, limonene, and multiple other low molecular weight compounds that improve the absorption properties of the peels, it was concluded from the results that both COP and ACOP were effective for completely removing the metals (Cd and Cr) from all the collected samples to collaborate the study of Perez-Marín*et al*., 2009, Mohamed and Amaal, 2017, Yin-Ling *etal*., 2010.

Funding

The research was fully funded by the corresponding author and the co-authors on a reasonable amount.

Conflict of Interest

The authors declare no competing interests on the research topic

Availability of Data and Materials

All the datasets generated during and/ or analyzed during the study were gotten from the research.

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	Website: www.ijarbs.com
Quick Response Code	Subject: Bioresources Technology.
DOI:10.22192/ijarbs.2024.11.10.001	

How to cite this article:
Fatukasi B. Adetutu, Fawole O. Olubanjo ,Ogunsona S.B, Olatunji, J.T and Ogunleke O.B. (2024). Application of Orange fruit peels for the adsorption of heavy metal concentrations in Asariver. Int. J. Adv. Res. Biol. Sci. 11(10): 1-10.
DOI: http://dx.doi.org/10.22192/ijarbs.2024.11.10.001