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Remediation of Water Contaminated with Cr⁶⁺ and Cd²⁺ Using Aluminophosphates Derived from Ashes of Tea Leaves and Pumpkin Seeds

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Abstract

Access to clean water is an ever increasing challenge that is not only fuelled by climate change and phenomenally growth in population but also by pollution by heavy metals arises from many sources that include automobiles, purification of metals, smelting industries, paint industries and textile industries. Water pollution is on the increase owed to industrial development and population increases. Commercial adsorbents frequently used as adsorbents in water remediation remain expensive out of reach to majority low income earners. It is therefore essential to develop cheap adsorbent materials capable of removing Cr^{6+} , Cd^{2+} ions and turbidity from wastewaters. Tea leaves ash (TLA) and pumpkin seeds ash (PSA) was used to generate aluminophosphates materials by hydrothermal reactions for removal of selected heavy metals from contaminated waters. Two adsorbents A and B were also prepared by varying ratios of TLA and PSA. Material A, (APA) was prepared by mixing TLA and PSA as in ratio of 1:1 while material B, (APB) was prepared by mixing them in ratio of 1:2. X-Ray diffraction was used for phase identification and characterization of synthesized material. The effects of metal ion concentration, initial pH, contact time, temperature, shaking speed and dosage on percentage removal of Cd⁺², and Cr⁺⁶ were determined. The equilibrium adsorption data fitted best in Langmuir isotherm model, as it had the highest value of correlation coefficient. Maximum monolayer adsorption capacities were 45.45 mg/g for cadmium and 50.00 mg/g for chromium using APA. Adsorption capacities of APB were 40.00 mg/g for cadmium and 41.67 mg/g for chromium. Based on adsorption capacities, APA was a better adsorbent than APB. The results from this study shows agro based aluminophosphates are potential adsorbents for remediation of heavy metals from waste waters.

Keywords: Adsorption isotherms, Heavy metals, Aluminophosphates, Wastewaters, Adsorbents

Introduction

The pursuit for technological advancement and industrialization has caused unexpected damages to our environment[¹]. Cadmium pollution has increased dramatically due to use of cadmium-containing products that are often dumped together with household waste[²]. Cadmium compounds are mainly used in re-chargeable nickel–cadmium batteries for electronic gadgets such as cell phones. Chromium salts are widely used by tannery industries and in recent years in large industrial application in textile dyeing, chemicals and pigments production, wood preservation, tanning activity and electroplating for surface treatment [3]. This has led to large quantities of the element being released to the surrounding environment. Cr^{6+} is one of the most dangerous environmental pollutants due to its ability to cause mutations and cancer in biological system. Being mutagenic, carcinogenic and teratogenic, Cr^{6+} is approximately 100-fold more toxic than Cr^{3+} [³]. The conventional technologies for the removal of heavy metals from waste waters include mainly chemical precipitation, ion exchange adsorption, membrane processes and evaporation that require high capital investment and running cost and hence not available among the poor[⁴]. It is therefore most desirable to explore possibilities of developing cheaper water treatment materials. The findings here in suggest that tea leaves and pumpkin seeds can be used as raw materials for synthesizing adsorbent materials for heavy metal removal from contaminated water.

MATERIALS AND METHODS

Chemicals

A stock solutions of cadmium and Chromium with a concentration of 1000 mg/L was prepared by dissolving 2.74 g of cadmium (ii) nitrate and 2.83g of potassium dichromate in 1000 mL distilled water in volumetric flask.

^[1]Bagul, V. R., Shinde, D. N., Chavan, R. P., Patil, C.L. (2015). Causes and Impacts of Water Pollution on Rivers in Maharashtra-A Review. *Res J. Chem. Environ. Sci.* 3[6] ISSN 2321-1040

^{[&}lt;sup>2</sup>]LarsJärup.(2003). Hazards of heavy metal contamination. Br Med Bull68 (1):167-182. doi: 10.1093/bmb/ldg032

^{[3}]Ferdouse, Z. T., Azizul, H., Sirajul, H. (2016).Bacterial Tolerance and Reduction of Chromium (VI) by Bacillus cereus Isolate PGBw4. *American Journal of Environmental Protection.5*(2): 35-38. doi: 10.11648/j.ajep.20160502.13.

^[4] Aksu, Z. (2002).Determination of equilibrium kinetic and thermodynamic parameters of the batch biosorption of Nickel (ii) ions onto *Chlorella Vulgaris*. *Process Biochemistry* 38: 89 – 99.

The solutions were then diluted to obtain working solutions containing 100mg/L and standard solutions of 0, 2, 4, 6, and 8 mg/L. The pH adjustment was done using a mixture of Na_2CO_3/HCl for cadmium and Na_2CO_3/H_2SO_4 for chromium⁸.

TLA and PSA preparation

Tea leaves were obtained from Muranga. They were then transported to the laboratory where they were extensively washed with tap water to remove dust, and then rinsed with distilled water and then air dried. Ashing was done using an oven at a temperature of 400°C for three hours. The ash was mixed to obtain a composite sample. Samples were sieved to obtain particles of the same size. Pumpkin seeds were obtained from pumpkin vendors in Molo. They were then washed several times with distilled water to remove soil and dust, followed and then dried at 100°C. The clean and dry pumpkin seeds were burnt in an oven at 800°C for 6 hrs. to obtain ash. The ash was mixed and sieved to obtain fine particles of the same size.

Synthesis of aluminophosphate material A, APA

30 g of TLA was mixed with 30 g of PSA. The mixture was put in 1000mL glass beaker and 400mL distilled water added. The mixture was stirred continuously. It was then transferred into stainless steel metallic cylinder. 100 mL 28% ammonia solution was added on this ash; the stainless steel was closed and introduced into a preheated oven at 100°C for a period of 24 hrs. The contents were then allowed to cool and filtered. The solid residue was washed with distilled water to remove the excess ammonia solution and dried at 100°C for 12 hrs. The solid residue was designated as APA.

Preparation of aluminophosphate material B, APB

For the preparation of APB, 20g of TLA and 40 g of PSA were put in a reaction bomb. 400 mL of distilled water was added to the mixture and stirred. The mixture was put in a digestion bomb and 100 mL of 28% ammonia added as a source of quaternary ammonium ion that acts as structure directing agent. The bomb was put in a preheated oven at 100°C for 24 hrs. The formed solid was washed with distilled water to remove the excess ammonia. It was then dried at 100°C for 12 hrs. The samples were designated as APB.

Batch experiments

A temperature-controlled water-bath shaker (DKZ-1 NO.1007827) was used for the batch adsorption experiments. The experiments were performed at the same shaking speed. For each experimental run, 50 mL aqueous solution of known concentrations of Cd²⁺and Cr⁺⁶ions were put in 100 mL plastic bottles that contained known masses of APA and APB. These bottles were agitated at a constant shaking rate of 420 rpm and temperature of 25°C, and filtered. The concentration of Cd²⁺and Cr⁺⁶ions in the filtrates obtained were measured using flame atomic adsorption spectrometry. Amount of Cd²⁺and Cr⁺⁶ions adsorbed per unit mass of adsorbent and their percentage removal were calculated using the equations 1 and 2 respectively.

$$q_{e} = \frac{C_{o} - C_{e}}{m} V - \dots - 1$$

$$R = 100 \frac{C_{o} - C_{e}}{C_{o}} - \dots - 2$$

Where,

 q_e = Amount of adsorbate ions adsorbed per unit mass of adsorbent at equilibrium.

 C_o = Initial concentration of sorbate.

 C_e = Concentration of sorbate at equilibrium.

m = mass of sorbate (g) (atomic mass).

V = volume of solution, (L).

Effect of the various parameters on the percentage of Cd²⁺andCr⁺⁶ions adsorbed

The effects of various parameters (adsorbent dose, contact time, initial concentrations, pH, shaking speed and temperature) on the percentage of Pb^{2+} ions adsorbed were investigated by varying the parameter of interest while keeping all the others constant. The effect of initial concentration was investigated by varying initial concentration from 20 to 500mg/L at same conditions of: 0.1g of adsorbents, temperature of $25^{\circ}C$, agitation speed of 420 rpm, and contact time of 60 minutes. The effect of the adsorbent dosage was investigated by varying the doses from 0.1 to 0.5g at same conditions of 100 mg/LCd²⁺ and Cr⁺⁶ion solutions for APA and APB and, agitation speed of speed of 420 rpm, temperature of 25°C and contact time of 60 minutes. The effect of contact time was investigated by varying contact time from 20 to 100 min at same conditions of: 0.1g of adsorbents, 100mg/L Cd²⁺ and Cr⁺⁶ion solutions of: 0.1g of adsorbents, 100mg/L Cd²⁺ and Cr⁺⁶ion solutions of: 0.1g of adsorbents, 100mg/L Cd²⁺ and Cr⁺⁶ion solutions of: 0.1g of adsorbents, 100mg/L Cd²⁺ and Cr⁺⁶ion solutions of: 0.1g of adsorbents, 100mg/L Cd²⁺ and Cr⁺⁶ion solutions for APA and APB and, temperature of 25°C, agitation speed of 420 rpm. The effect of pH was investigated by varying pH from 2 to 6 at same conditions of: 0.1g of adsorbents,

 100mg/LCd^{2+} and Cr^{+6} ion solutions for APA and APB, temperature of 25°C , agitation speed of 420 rpm, contact time 60minutes. The shaking speed was investigated by varying shaking speed from 120 to 600 rpm at same conditions of: 0.1g of adsorbents, 100mg/LCd^{2+} and Cr^{+6} ion solutions for APA and APB and, temperature of 25°C . The effect of temperature was investigated by varying the temperature from 20 to 100°C at same conditions of: 0.1g of adsorbents, 100 mg/LCd^{2+} and Cr^{+6} ion solutions for APA and APB and, agitation speed of 420 rpm and contact time of 60 minutes.

RESULTSAND DISCUSSIONS

Samples characterization

Chemical analysis of TLA and PSA was done using EDX spectroscopy and the major oxides found are shown in tables 1 and 2 respectively. The proportion of aluminum oxide in ash from old tea leaves was found to be about 30% in agreement with literature data reported by Dong *et al.* (1999)[¹].

Compound	K ₂ O	Al_2O_3	SiO ₂	Cl	Fe ₂ O ₃	P_2O_5	CaO	SO ₃	TiO ₂
wt%	49.42	30.09	6.24	4.34	3.30	2.62	1.78	1.36	0.31
Compound	ZnO	MnO	ZrO_2	Rb ₂ O	Br	SrO	NbO	Y_2O_3	
wt%	0.22	0.21	0.05	0.04	0.02	0.01	0.011	0.004	_

Table 1: Chemical oxide composition from EDX analysis oftea leaves ash

The ash from pumpkin seeds contained approximately 37% of P_2O_5 confirming that it can serve as asource of phosphate. The presence of K_2O in proportions of about 49 and 44% in TLA and PSA respectively is important as it provides alkali conditions necessary for the hydrothermal reaction.

Compound	K ₂ O	P_2O_5	Fe ₂ O ₃	SiO ₂	CaO	SO ₃	ZnO	
wt%	43.62	37.01	8.32	4.42	3.68	1.41	0.82	
Compound	MnO	SeO ₂	CuO	Rb ₂ O				
wt%	0.40	0.14	0.10	0.08				

Table 2: Chemical oxide composition from EDX analysis of pumpkin seeds ash

Characterization of aluminophosphate materials APA and APB

The X-ray diffraction pattern shown in figure 1 confirmed the presence of Kaolinite (20.9%), smectite (6.7%), AlPO-8 (34.1%), quartz (12.6%), ilitite (2.3%) and amorphous (23.4%) in APA⁹. The X-ray diffraction pattern of APB shown in figure 2 indicated that it contained kaolinite (15.6%), smectite (4.4%), AlPO-H2 (28.7%), ilitite (2.2%), Quartz (20.1%) and AlPO-C (5.2%) minerals. This implies that the ash mix ratio is a key factor in determining the mineral composition of the hydrothermal product.



[¹]Dong, D., Xie, Z., Du, Y., Liu, C. and Wang, S. (1999). Influence of soil pH on aluminum availability in the soil and aluminium in tea leaves. *Communication in Soil Science and Plant Analysis* 30: 873–883.





Effects of PH on percentage removal of Cd²⁺ and Cr⁺⁶ ions

The effect of varying the pH from 2 to 6on the percentage removal of Cd²⁺ and Cr⁺⁶ionsby APA and APB areshown in figures 3 and 4 respectively. The percentage removal of Cd²⁺by APA increased from 72.3% at pH 2 to 75.5, 77.8 and 93.3 at pH of 3, 4 and 5 respectively. The percentage removal by APB increased slightly from 77.9 to about 80 at pH of 3 and 4 then attained equilibrium at a pH of 5. At low pH, surface of adsorbents are protonated, thus there is repulsion between the surface of adsorbent and Cd^{2+} decreasing the rate of adsorption[¹]. As pH increases active sites are less protonated increasing the attraction between the adsorption sites and cadmium ions. Thereafter, the percentage removal of Cd²⁺ remained constant with increase in PH. This was as a result of exhaustion of active sites. In case of Cr^{6+} ions, the percentage removal when using the adsorbent APA dropped from over 96% at pH of 2 to 94% at pH of 4 while when using APB the percentage removal dropped from over 95% at pH of 2 to 62% at pH of 6. Decreasing pH results in the formation of more polymerized Cr oxide species. On the other hand, under acidic conditions, the surface of the adsorbent becomes highly protonated and favors the uptake of Cr⁶⁺ in the anionic form. When the pH is increased the degree of protonation of the surface reduces gradually and hence adsorption is decreased[2]. Moreover, as pH increases there is competition between OH⁻ and chromate ions (CrO_4^{2-}), the former being the dominant species at higher pH values. The net positive surface potential of sorbent decreases, resulting in the weakening of electrostatic forces between sorbent and sorbate, which ultimately leads to reduced sorption capacity^[3].

^{[&}lt;sup>1</sup>]Zheng, L., Zhu, C., Dang, Z., Zhang, H., Yi, X. and Liu, C. (2012). Preparation of cellulose derived from corn stalk and its application for cadmium ion adsorption from aqueous solution. *Carbohydrate Polymer*90(2): 1008-1015.

^{[2}]Selvi, K., Pattabhi, S., Kadirvelu, K. (2001). Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon.*Bioresources Technology* 80: 87–89.

^{[3}]Cimino, G., Passerini, A. and Toscano, G. (2000).Removal of toxic cations and Cr (VI) from aqueous solution by hazelnut shell.*Water Research*34: 2955-2962.



Figure 3: Effect of pH on the removal of Cd^{2+} and Cr^{6+} ions by APA (Adsorbent dose = 0.1g, agitation speed = 420 rpm and temp = $25^{\circ}C$)



Figure 4: Effect of pH on the removal of Cd^{2+} and Cr^{6+} ions by APB (Adsorbent dose = 0.1g, agitation speed = 420rpm and temp = 25°C).

Effect of contact time on percentage removal of Cd²⁺ and Cr⁶⁺ions

Experiments were conducted by, varying contact time from 20 to 100 min while maintaining all other experimental conditions constant. The results obtained are shown in Fig. 5 and 6. As shown the adsorption process occurred rapidly when APA and APB were used with over 79% of the Cd^{2+} ions present adsorbed by APA and over 74% for APB after 20min. APA achieved over87% removal after 80min and reached equilibrium within 80min while APB achieved 74.4% removal after 20 min, then increased to 81.3% at 80 min after which it remained constant. Percentage removal of Cr^{6+} using APA was over 94% after 20 min and increased slightly with time while when APB was used the percentage removal increased from 50% to over 76% within the duration of 20 to 100 min. There was an increase rate of adsorption with increase in contact time. Increase in contact time increased the chances of interaction between adsorbate ions and adsorbent sites increasing the rate of adsorption. Equilibrium is attained after exhaustion of the active sites present in the adsorbents[¹].



Figure5: Effect of contact time on the removal of Cd²⁺ and Cr⁶⁺ions by APA (Adsorbent dose = 0.1g, agitation speed = 420rpm and temp = 25^oC)

^{[&}lt;sup>1</sup>]Mirghaffari, N., Moeini, E., Farhadian, O. (2015).Biosorption of Cd and Pb ions from aqueous solutions by biomass of the green microalga, Scenedesmusquadricauda.*J. Appl.Phycol*27: 311–320.



Figure6: Effect of contact time on the removal of Cd^{2+} and Cr^{6+} ions by APB (Adsorbent dose = 0.1g, agitation speed = 420rpm and temp = 25°C)

Effect of adsorbent dosage on adsorption of Cd²⁺ and Cr⁶⁺ions

Experiments were conducted with the adsorbent dose of 0.1, 0.2, 0.3, 0.4 and 0.5g per 50mL of test solution. When the addition of the adsorbent dose increased, the percentage removal of metal ions also increased as shown in fig 7 and fig 8. Percentage removal of Cd^{2+} increased from 89.4% at a dose of 0.1g to almost 100% at 0.2g using APA and 80.8% at adsorbent dose of 0.1g to 89.2% and almost 100% at adsorbent dose of 0.2 and 0.3g respectively when using APB. For Cr^{6+} the mean percentage removal increased from 94.35 to 97.66 and almost 100% for dose of 0.1, 0.2 and 0.3g respectively using adsorbent APA while when using APB the percentage removal changed from 73.5 to 83.1 and almost 100% at adsorbent dose of 0.1, 0.2 and 0.3grespectively.Adsorption of Cd^{2+} and Cr^{+6} ions increased due to increase in number of binding sites as the adsorbent dose increased [1]. A further increase in adsorbent dose did not have any significant effect on the removal of metal ions from the solution because the adsorbate ions are already exhausted.



Figure 7: Effect of adsorbent dose on the removal of Cd^{2+} and Cr^{6+} ions by APA (contact time = 60 min, agitation speed = 420rpm and temp = $25^{\circ}C$)



Figure 8: Effect of adsorbent dose on the removal of Cd²⁺ and Cr⁶⁺ions by APB (contact time = 60 min, agitation speed = 420rpm and temp = 25^oC)

Effect of shaking speed on percentage removal of Cd^{2+} and Cr^{6+} ions The percentage removal of Cd^{2+} and Cr^{+6} ions were determined while varying the shaking speed from 120 to 600rpm and presented in figures9 and 10. The percentage removal of cadmium (II) was found to be 83.8% at 120rpm then increased to 91.6% at shaking speed of 600rpm when using adsorbent APA. When APB was used the percentage removal changed from 82.9% at 120rpm to 84.9 at 600rpm. For chromium (VI) ions the percentage removal increased slightly from 94.08% at 120rpm to 95.9% at 480rpm and remained constant when APA was used. For APB the percentage removal dropped from 68.2% at 120rpm to 75.5% at 600 rpm. At low shaking speed, the adsorbent accumulates and various active sites are buried under the above layer reducing the rate of adsorption. Increase in the shaking speed improves the diffusion of metal ions towards the surface of the adsorbent[¹]. It also helps in spreading the sorbent surface making the active sites available for adsorption and this increases the rate of adsorption.



Figure 9: Effect of shaking speed on the removal of Cd^{2+} and Cr^{6+} ions by APA (Adsorbent dose = 0.1g, agitation speed = 420 rpm and temp = 25°C).



Figure 10: Effect of shaking speed on the removal of Cd^{2+} and Cr^{6+} ions by APB (Adsorbent dose = 0.1g, agitation speed = 420rpm and temp = 25°C).

Effects of temperature on adsorption of Cd²⁺ and Cr⁶⁺ ions

The effect of temperature on the removal of Cd^{2+} and Cr^{+6} ions by APA and APB at initial solution concentration of 100 mg/L of Cd^{2+} and Cr^{+6} ions solution using 0.1 g and contact time of 60min and agitation speed of 420rpm are shown in figure 11 and 12. From the results, it was observed that the percentage removal of Cd^{2+} and Cr^{+6} ions by APA and APB remained constant with increase in temperature from 20 to 40^oC. There was a rapid decrease in percentage removal of Cd^{2+} and Cr^{+6} ions by APA and APB when the temperature was increased

^[1] Mehmet, E.A.,Sukru, D.,Celalettin, O. and Mustafa, K. (2007).Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics. *Journal of Hazardous materials* 141:77-85.

from 40 to 100° C. The observed initial decrease in Cd²⁺ and Cr⁺⁶ ions removal with increasing temperature suggests weak binding interaction between the active sites and metal ions which support physiosorption which are exothermic and therefore favoured by low temperature.



Figure 11: Effect of temperature on the removal of Cd^{2+} and Cr^{6+} ions by APB (Adsorbent dose = 0.1g, agitation speed = 420 rpm and temp = 25°C).



Figure 12: Effect of temperature on the removal of Cd^{2+} and Cr^{6+} ions by APB (Adsorbent dose = 0.1g, agitation speed = 420 rpm and temp = $25^{\circ}C$).

Effect of the initial concentrations of Cd^{2+} and Cr^{+6} ions

The percentage of Cd^{2+} and Cr^{+6} ions adsorbed by APA and APB were significantly influenced by the initial concentration of metal ions in aqueous solutions. The initial Cd^{2+} and Cr^{+6} concentrations were varied from 20mg/L to 500mg/L while maintaining the adsorbent dosage at 0.1g. Figures13 and 14 show the effects of initial concentration on percentage removal of Cd^{2+} and Cr^{+6} ions by APA and APB respectively. The percentage removals of Cd^{2+} and Cr^{+6} decreased from about 100% to 19.9% and 100% to 16.5% respectively for APA, about100% to 18% and about100% to 16.1% respectively for APB at the same contact time and adsorption temperature. Increase in concentration lead to a decrease in percentage removal of Cd^{2+} and Cr^{6+} ions due to an increase in the number of metal ions for the fixed amount of adsorbent.



Figure 13: Effect of initial solution concentration on the removal of Cd²⁺ and Cr⁶⁺ ions by APA (amount of adsorbent = 0.1g, contact time = 60 min, agitation speed = 420rpm and temp = 25^oC)



Figure 14: Effect of initial solution concentration on the removal of Cd²⁺ and Cr⁶⁺ ions by APB (amount of adsorbent = 0.1g, contact time = 60 min, agitation speed = 420rpm and temp = 25^oC)

Langmuir and Freundlich isotherm constants for adsorption of cadmium and chromium ions

The adsorption data for Cd^{2+} and Cr^{6+} by both APA and APB at the various initial concentrations were fitted into Langmuir and Freundlich isotherms and the constants obtained summarized in table 3.As indicated in the table, adsorption data for Cd^{2+} on both APA and APB was found to best fit into Langmuir model as implied by the R²values of0.999 for both adsorbents against Freundlich values of 0.113 and 0.054 for APA and APB respectively. Similarly adsorption data for Cr^{+6} best fitted into Langmuir model with R² values of 1 and 0.999 for APA and APB respectively. This indicates a monolayer sorption onto adsorbent surfaces that contain finite number of identical active sites.APA had the highest affinity for Cd^{2+} and Cr^{+6} ions with adsorption capacity, q_{max} of about 45.5 and 50.0mg/g respectively. The adsorption capacity of APB was 40.0 and 41.7 mg/g for Cd^{2+} and Cr^{+6} ions respectively. The study showed that APA and APB effectively remove Cd^{2+} and Cr^{6+} ions from contaminated water.

Table 1: Langmuir and Freundlich isotherm constants for Cd²⁺ and Cr⁶⁺ions

	Freundlich						
Metal ions	Adsorbents	q _{max} mg/g	b dm³/g	\mathbf{R}^2	1/n	K _f mg/g	\mathbf{R}^2
Cd	APB	40.0	4.17	0.999	0.004	39.4	0.113
Cd	APA	45.5	0.47	0.999	0.006	42.2	0.054
Cr	APB	41.7	0.96	0.999	-0.034	48.8	0.636
Cr	APA	50.0	2.22	1	0.01	46.8	0.923

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