BIOSORPTION OF Cr^{3+} AND Pb^{2+} FROM TANNERY WASTEWATER USING COMBINED FRUIT WASTE

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Abstract. In recent years, tanning industries have been proved to be among the major contributors of heavy metals. Different convectional and biological method has been used to remove these heavy metals from tannery wastewater but most of these technologies are costly and not easily accessible. This research is aimed at determining the efficiency of combining the waste rind of *Citrulus lanatus* and waste peel of *Citrus sinensis* as a low cost biosorbent for the removal of Cr^{3+} and Pb^{2+} pollutants present in tannery wastewater. The selected biosorbents where surface characterized and point of zero (pH_{PZC}) was determine with pH adjusted using NaOH solution to be between 2-12. The adsorption process of Cr^{3+} and Pb^{2+} by the selected biosorbent was determined under factors such as contact time, pollutants dosage, absorbent dosage, and particle size. The Lagmuir equation and Freundlich isothermal were used to determined adsorption equilibrium while pseudo first order and pseudo second order were used to determine the adsorption kinetics. The result obtained shows that *Citrulus lanatus* has better adsorption of Pb^{3+} (86%) while the combined fruit better adsorption of Cr^{3+} (85%) under the all factors. The Lagmuir equation and Freundlich shows suitability of indicating equilibrium sorption for Cr^{3+} and Pb^{2+}. The adsorption kinetic study shows that pseudo-second order obeys kinetics model signifying that absorption occurs by chemisorptions. The combination of the waste rind of *Citrulus lanatus* and waste peel of *Citrus sinensis* is an effective low cost biosorbent for the removal of Cr^{+3} and Pb^{+2} pollutants present in tannery wastewater.
Keywords: *adsorption isotherm, heavy metal pollution, adsorption kinetics, Citrus sinensis, Citrulus lanatus*

Introduction

Heavy metal pollution resulting from anthropogenic activities is a serious problem to man and his environment due to the persistence nature and ability of heavy metals to accumulate in the food chain (Dudgeon et al., 2006; Lintern et al., 2016; Liu et al., 2018). In developing countries, industries channel wastewater into nearby water bodies either untreated or not properly treated due to their proximity to these water bodies (Desrosiers et al., 2019).The wastewater produce by most of these industries are rich in heavy metals which pose serious toxicity at low level exposure (Hughes et al., 2015). In recent years, tanning industries have been proved to be among the major contributors of heavy metals (Cr, Pb, Zn, Cu, Cd, As and Se) in to water bodies (Aravindhan et al., 2004; Di Iaconi et al., 2003; Panizza and Cerisola, 2004). These heavy metals release into water bodies have been shown by many researchers to be associated with chronic and acute effects to man and detrimental to other organisms such as algae, plants, other animals, microorganisms etc (Costa-Boeddeker et al., 2018; Wang et al., 2018; Xun et al., 2018). It is thereby paramount to treat wastewater before discharge (Tong and Elimelech, 2016; Zhang and Anadon, 2013).

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A lot of technology is available for the treatment of wastewater before discharging into water bodies, many of which have contributed in minimizing pollution resulting from chemical industries but biosorption is gaining acceptance owing to the fact that most researchers have reveal the potentiality of some bio sorbents to effectively remediate wastewater with high heavy metal pollutants removal if match up to other biological and conventional technologies (Nahar et al., 2018). Biosorption is a remediation technology that depends on the mechanism of heavy metal accumulation by agricultural or biological adsorbents from an aqueous solution as a result of binding site present on this bio sorbents (He and Chen, 2014; Ileri et al., 2014).

Several research have been conducted showing the efficiency of different biosorbent removing Cr^{3+} from wastewater among which include egg-shell, sawdust, rice husk and lemon peel (Nahar et al., 2018), phosphate treated sawdust (Ajmal et al., 1996), cotton hull and soybean (Marshall and Champagne, 1995), sawdust carbon (Selvi et al., 2001), egg-shell (Park et al., 2007; Mashangwa et al., 2017), Litchi peel (Manikandan et al., 2016), modified groundnut hull (Owalude and Tella, 2016), Powdered potatoes peel (Mutongo et al., 2014), *Citrus limetta* (Saha et al., 2013) etc.

Nevertheless, Pb^{2+} has also attracted researchers for use in the biosorption of wastewater. This curiosity have led to the success of the used of different agricultural waste as low-cost biosorbents, among which include banana peel (Anwar et al., 2010), different cortex fruits (Al-Qahtani, 2016), Agare bagasses (Velazquez-Jimenez et al., 2013), Garden grass (Hossain et al., 2012), modified orange peel (Guo et al., 2011), modified lentic husk (Basu et al., 2015), olive stone raw (Fiol et al., 2006), ponkan peel (Pavan et al., 2008) etc.

A lot of success has been recorded for the biosorption of different pollutants by *Citrus sinensis* (Feng et al., 2011; Guiza, 2017; Pérez-Marín et al., 2008) and *Citrulus lanatus* (Reddy et al., 2014; Liu et al., 2012; Jawad et al., 2018), however more research is needed to investigate how those agricultural wastes can be improved for effective pollutants removal from waste water. The current research is aimed at determining the efficiency of combining the waste rind of *Citrulus lanatus* and waste peel of *Citrus sinensis* as a low cost biosorbent for removal of Cr^{3+} and Pb^{2+} pollutants present in tannery wastewater.

Material and Method

Sample Collection and Preparation

The waste peel of C*itrus sinensis* peel and *Citrulus lanatus* rind were collected from road side fruit sellers at kasuwan mata, Kaduna South Local Government, Kaduna State, Nigeria. Both bio-wastes were cut into small pieces, washed several times with borehole water then distilled water. *Citrus sinensis* peel was dried at 40°C in the oven as described by Kelly-Vargas et al. (2012). *Citrulus lanatus* rind was first dried in sunlight for 48 hours then oven dried at 80°C. The fruit wastes were grounded using a mechanical blender (Greenis, FGR-8840) and then sieved through standard sieve to obtain various size of C*itrus sinensis* peel and *Citrulus lanatus* rind. The fruit waste powders were stored separately in an airtight container before use. To obtain a combined fruit waste of the two peels, an equal amount of dried, grounded peels were weighed and mixed together. Tannery effluent samples were collected from the main discharge point/network pipeline of Unique Leather Industry located at Sharada industrial area, Kano. Standard sample bottles were used in collecting the wastewater

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sample. Using distilled water, the bottles were washed thoroughly. The samples were placed in an storage box containing ice packs in order to preserve and maintain their composition thus preventing degradation by microbes. In this regard, each sample bottle is added with 5 ml 2.0 M nitric acid per litre (Lugo-Lugo et al., 2012). Digestion of samples was carried out according to the Standard method by Ahuja (2012). Samples were filtered using Whatman filter paper of pore size 0.45µm and analysed using AAS for heavy metal content as described by Lugo-Lugo et al. (2012). pH was measured using Toledo pH meter of model FE20/EL 20.

Characterization of Biosorbents

Citrus sinensis peel, *Citrulus lanatus* rind and Combine fruit waste were pre-treated using H_2O_2 according to Shen et al. (2011). Surface characterization was done using the method of Boehm (1966) in which 0.4g of *Citrus sinensis* peel, *Citrulus lanatus* rind and Combine fruit waste was were neutralize separately using 50ml of Cr^{+3} and Pb^{+2} solution by using acid based titration techniques for 5 days. Point of zero (pH_{PZC}) of *Citrus sinensis* peel, *Citrulus lanatus* rind and Combine fruit wastewater determined by adjusting the pH value using 50ml 0.01 NaCl solution to between 2-12. The samples were agitated and stored for 24 hours at 12rpm at room temperature. The P_{PZC} was then calculated graphically according to Banerjee et al. (2017). Scanning electron microscope (JEOL JSM-6100) was used to observe how the surface of *Citrus sinensis* peel, *Citrulus lanatus* rind and Combine fruit waste is affected by the adsorption process.

Effect of Particle Size and Contact Time on Cr and Pb Adsorption

The effect of contact time and particle size was studied together by placing 5g of *Citrus sinensis* peel, *Citrulus lanatus* rind and Combine fruit waste of two particle sizes (40mm (coarse) and 60 mm (fine)) in separate conical flasks containing 100 ml effluent sample and agitated at 150 rpm in a shaker. Each set of flasks were agitated for 20, 40, 60, 80, 100, and 120 minutes, respectively. The samples were filtered using Whatman No 41 filter paper after each interval. Residual heavy metal concentration of the sample was measured, using AAS.

Biosorption was calculated using the mass balance formula below:

$$q = \frac{v(C_l - C_e)}{m} \quad \text{(Eq.1)}$$

where, q (mg/g) is the adsorption capacity, C_l and C_e are the initial and final concentrations (mg/l) of sample, V(l) is the volume of effluent sample and m is the weight (mass) of adsorbent (g).

Percentage removal: it was calculated using the formula:

$$q\%\ uptake = \frac{(C_o - C_e)}{Co} \times 100 \quad \text{(Eq.2)}$$

where C_0 and C_e are the initial and final concentrations (mg/l) of metals in sample before and after shaking.

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Effect of Cr^{3+} and Pb^{2+} dosage on Adsorption Process

To the 250 m/l of solution containing 15 mg/l, 20 mg/l, 25 mg/l, 30 mg/l and 35 mg/l Cr and 10 mg/l, 15 mg/l, 20 mg/l, 25 mg/l and 30 mg/l of Pb 5g of dried *Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combined fruit waste was added separately and shaked at room temperature at 150 rpm for 12 hours. Cr and Pb percentage reduction was thus calculated using the method employed by Kumar et al. (2018).

Percentage removal: it was calculated using the *Equation 2*.

Effect of pH on Cr and Pb adsorption Process

The absorption ability of the solvent was compared at a pH of 2, 4, 6, 7, 8 by placing 1g of *Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combined fruit waste in 100 ml each of the solution of Cr and Pb at 15 mg/l and 10 mg/l, respectively. The samples were filtered using Whatman No 41 filter paper after each interval. Residual heavy metal concentration of the sample was measured, using AAS. The pH of the solution was adjusted using diluted sodium hydroxide and Nitric acid as adopted from Salim et al. (2016).

Effect of Particle Size and Dosage

The effect of absorbent dosage was study by dissolving a fixed mass of 15mg/l of Cr^{3+} and a fixed mass of Pb^{2+} 10 mg/l in 100 ml of solution. 1 g, 2 g, 3 g, 4 g and 5 g each of *Citrus sinensis* peel, *Citrulus lanatus* rind, and combined fruit waste where placed in each solution. The samples were filtered using Whatman No. 41 filter paper after each interval. Residual heavy metal concentration of the sample was measured by using AAS as described above.

Adsorption Equilibrium Study

Adsorption equilibruim study for Cr and Pb using *Citrus sinensis* peel, *Citrulus lanatus* rind and hybrid fruit waste powder was performed by suspending 1g, 2g, 3g, 4g and 5g of *Citrus sinensis* peel, *Citrulus lanatus* rind and combined fruit waste powder in 15mg/l, 20mg/l, 25mg/l, 30mg/l and 35mg/l Cr^{+2} and 10mg/l, 15mg/l, 20mg/l, 25mg/l and 30mg/l of Pb^{+2} and shaked at room temperature at 150 rpm for 12 hours. Langmuir and Freudlich isotherm models were thus tested according to the method adopted by Manikandan et al. (2016).

Langmuir equation is represented below:

$$\frac{1}{q_x} = \frac{1}{b_i q_f} T_e + \frac{1}{q_f} \qquad \text{(Eq.3)}$$

The equation was adopted from Kumar et al. (2018), where T_e = Equilibrium Cr^{3+} and Pb^{2+} concentration in solution (mg/l), q_f is maximum Cr^{3+} and Pb^{2+} absorbed per unit weight of *Citrus sinensis* peel, *Citrulus lanatus* rind and combined fruit waste powder (mg/g), b_i is affinity adsorbate – biosorbent (l/mg), = is the amount of Cr^{3+} and Pb^{2+} adsorbed by the adsorbent at equilibrium (mg/g) the value of q_f and b_i is determined from the slope and intercept of. Z is the separation factor and is calculated using the formula below:

$$Z = \frac{1}{1 + b_I T_a} \qquad \text{(Eq.4)}$$

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where T_g = initial concentration of Cr^{+3} and Pb^{+2} in the solution.

Freundlich Isotherm is represented below:

$$Log\, qx = Log\, Kf + \frac{1}{r\, log\, T_e} \quad \text{(Eq.5)}$$

The equation was adopted from Wang et al. (2010), where K_f is Freudlich Constant *r* is Freudlich Coefficient, and K_f and *r* are determine by plotting a graph of q_x against T.

Adsorption Kinetics

Adsorption kinetics is fundamental in describing the characteristic of an absorbent. To ascertain the mechanism involve in the adsorption of Cr^{3+} and Pb^{2+} by *Citrus sinensis* peel, *Citrulus lanatus* rind and combined fruit. Pseudo first order and pseudo second order reaction was used according to the procedure of Ho and McKay (1998).

The pseudo first order is represented below:

$$Log\ (q_i - q_t) = log\ (q_i) - \frac{K_i T}{2{,}303} \quad \text{(Eq.6)}$$

The equation was adopted from Poonam et al. (2018), where q_i and q_t = Amount of Cr^{3+} and Pb^{2+} (mg/g^{-1}) absorbed at equilibrium and time *T*, respectively, *K* is the pseudo-first order rate constant (min^{-1}).

The pseudo second order is represented below:

$$\frac{T}{q_t} = \frac{1}{K_2 q_2} + \frac{T}{q_2} \quad \text{(Eq.7)}$$

$$\frac{1}{q_t} = \frac{1}{K_2 q_2 T} + \frac{1}{q_2} \quad \text{(Eq.8)}$$

The equation was adopted from Poonam et al. (2018), where q_i and q_t = Amount of Cr^{3+} and Pb^{2+} (mg/g^{-1}) absorbed at equilibrium and time *T*, respectively, K_2 is the pseudo second order rate constant (g mg^{-1} min^{-1}).

Desorption Study

Desorption of Cr^{3+} and Pb^{2+} was from *Citrus sinensis* peel, *Citrulus lanatus* rind and combined fruit waste powder was studied for 0.1 N HCl, 0.1 N HNO_3, 0.1 N H_2SO_4 and 0.1 N NaOH. The dried *Citrus sinensis* peel, *Citrulus lanatus* rind and combined fruit waste powder with absorbed Cr^{3+} and Pb^{2+} in the solvents and shake for 150 rpm at room temperature for 12 hours adopted from Rosales et al. (2016). In order to determine the mechanism involve in adsorption of Cr^{3+} and Pb^{2+} by *Citrus sinensis* peel, *Citrulus lanatus* rind and hybrid fruit waste.

Statistical Analysis

Experimental was conducted in triplicate and data were analyzed statistically using standard deviation to find significance difference at 5% level. The Residual Sum of Squares (RSS) was determined for both adsorption kinetic and isotherm models to check error in model fittings. All analysis was done using BM SPSS statistics version 23.

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Result and Discussion

Effect of Contact Time on Cr^{+3} and Pb^{+2} Adsorption

Figure 1 shows the uptake of the two metal ions, Cr^{3+} and Pb^{2+} the waste peels (C*itrus sinensis* waste peel, *Citrulus lanatus* waste rind and combine fruits waste) was effective and continued progressively at the various time intervals set for the experiment. However, at 80 min the uptake of both metals stopped.

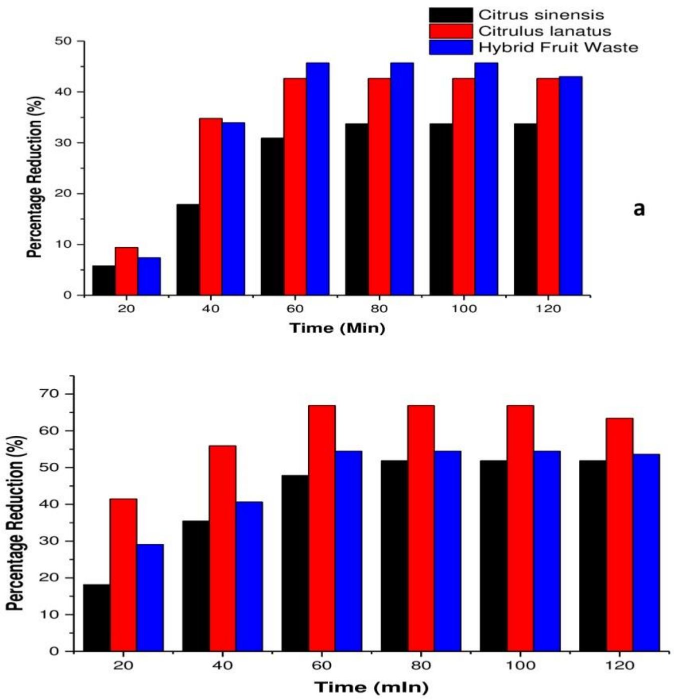

Figure 1. *Effect of Contact Time on Adsorption Cr^{+3} (a) and Pb^{+2} (b)*

The situation remained same from 100 min to 120 min. In other words, there was no net uptake of the metals after 80 min. The reason why the uptake of both Cr^{3+} and Pb^{2+} stopped from 80 min could be attributed to the fact that the particles of C*itrulus lanatus* waste rind, *Citrus sinensis* and the combined fruit waste peel posses selective potential for retaining of some heavy metals over a period of time (Ahad et al., 2017). With respect to contact time it is ascertain that Combined fruit waste was best in Cr^{3+} removal and *Citrulus lanatus* best in Pb^{2+} removal at all time interval used for the studies. This could be attributed to their surface areas. *Citrulus lanatus* waste rind and the combine waste fruit particles have a high surface area compare to *Citrus sinensis* waste peel thus providing more binding sites for metal ions. In contrast, *Citrus sinensis* has lesser surface area as such fewer sites for attachment by metal ions are available. Although, there was loss of metals at 120 min from the combine waste materials, it is likely that there was a synergistic effect by *Citrulus lanatus* and combine fruit waste (Gupta and Garg, 2015). The uptake of Cr^{3+} and Pb^{2+} also varied with size of the absorbent as higher uptake was noticed by fine absorbent (40mm) compare to coarse absorbent (60mm). The result obtained attribute high Pb^{2+} adsorption to fine particle of *Citrulus*

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lanatus if compare to coarse particle of *Citrulus lanatus*. The adsorption of Cr^{3+} by fine particles of combine fruit waste peel also follow the same trend as *Citrulus lanatus* if compare to coarse particle of combine fruit waste peel. The reason for the differences of pattern of adsorption of Pb^{2+} and Cr^{2+} by the absorbents based on size could be attributed to the fact that as the particle size increase so do the binding site increase resulting in the enhancement of metal absorption by the biosorbents (Al-Ghouti et al., 2003). Although, Senthil Kumar et al. (2012) shows that decrease of absorbent to a diameter of 240µm can cause reduction in adsorption ability of the adsorptive sites due to agglomeration of the particles that is not the case here because the lowest size used was 40mm.

Characterization of Biosorbents

Active site and surface area increase was recorded for *Citrus sinensis, Citrulus lanatus* and combined waste fruit waste peel although no significant differences (*P* = 0.05) exist between the increase of active sites and surface area of *Citrulus lanatus* rind compare to combine fruit waste but significant difference exist (0.05) between the increase of binding site and surface aarea of *Citrulus lanatus* rind and combined fruit waste compare to *Citrus sinesis* with both *Citrulus lanatus* and Combine fruit waste having more binding site and larger surface area. The pH (pH_{ZPC}) *Citrus sinensis, Citrulus lanatus* and combined waste fruit waste peel were 3, 4 and 7, respectively for Cr^{3+} but 2, 5, 4 for Pb^{3+}. The increase in active site and surface area is attributed to the collapsing of the adsorbent wall resulting to the modification of the adsorbent structure into porous structure. Result of scanning electron microscopic shows smooth surfaces for all the absorbent before adsorption study but rough surfaces after adsorption. The rough surface after adsorption signifies enhancement in adsorption capacity of the adsorbents and also the reason for the increase surface area.

Effect of Adsorbent Dosage on Cr^{+3} and Pb^{+2} Adsorption

Variation in dosage of *Citrus sinensis, Citrulus lanatus* and combined waste fruit waste peel affected the percentage uptake of Cr and Pb. Increase in dose of the test material from 1 – 5 g, was signified by an increase in percentage uptake of both metal ions (*Figure 2*). This could have resulted from the availability of more binding sites with each addition of waste materials. The difference in percentage uptake of Cr^{3+} by *Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combine waste rind was significant ($P < 0.05$) with combine waste fruit waste performing better than *Citrus sinensis* and *Citrulus lanatus*. The difference was also significant between *Citrus sinensis* waste peel, Citrulus lanatus and combines fruit waste for Pb^{2+} uptakes with *Citrulus lanatus* performing better than combined fruit and *Citus sinensis*. The reason could be similar to the same reason why both test material display the pattern of metal uptake under different duration.

Effect of pH on Adsorption Process

The adsorption process for Cu^{3+} and Pb^{2+} follow the decreasing pattern from pH of 2-12 with combine fruit waste material having higher adsorption for Cr^{2+} at the pH of 2 and *Citrulus lanatus* having higher adsorption for Pb^{2+} at pH of 2, pH was determined for these studies owing to the fact that Wang and Chen (2009) reported that the reason why biosorption occur is due to exchange of ion of which pH is the determinant factor

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for which proton compete with cation for binding sites (*Figure 3*). The higher adsorption recorded at the pH of 2 by all the materials used could be attributed to the fact that at lower pH (acidic medium), the removal of H^+ lead to availability of free binding sites for Cr^{3+} and Pb^{2+} (Poonam et al., 2018). Elhafez et al. (2017) had earlier reported that the removal of heavy metal by biosorption increases with increasing pH and decreases after pH of 4. This increasing pH tend to facilitate the precipitation of heavy metals thereby contributing to it removal.

Effect of Cr^{3+} and Pb^{2+} Dosages on Adsorption Efficiency

The test for the effect of Cr^{3+} and Pb^{2+} on adsorption efficiency was carried out taking into consideration the concentration of both heavy metals in the wastewater for effective treatment. The result obtain shows decreasing trend of adsorption efficiency with increase in mass of Cr^{3+} and Pb^{2+} ion concentration (*Figure 4*). This trend could be attributed to the fact that the increases in the concentration of Cr^{3+} and Pb^{2+} lead to decrease in the availability of free binding site on the solvent until the binding sites are completely saturated (Poonam et al., 2018; Zhang et al., 2018; Zhao et al., 2018). The difference in adsorption capacity of Cr^{3+} by *Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combine waste rind was significant at the different Cr^{3+} and Pb^{2+} concentration ($P < 0.05$) with combine waste fruit waste performing better than Citrus sinensis and Citrulus lanatus in Cr^{3+} adsorption and Citrulus lanatus performing better in Pb^{2+} adsorption.

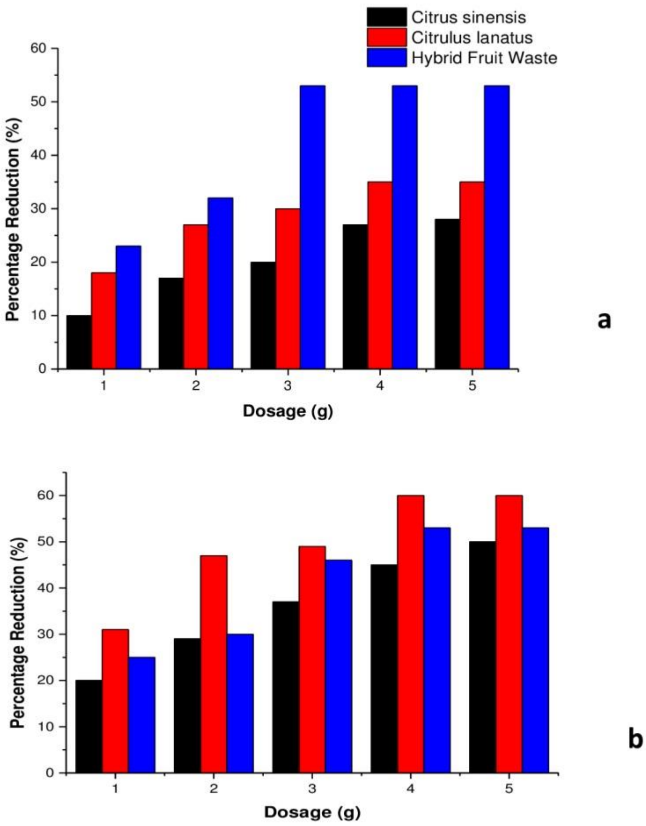

Figure 2. *Effect of Adsorbent Dosage on Adsorption (a) Cr^{3+} (b) Pb^{2+}*

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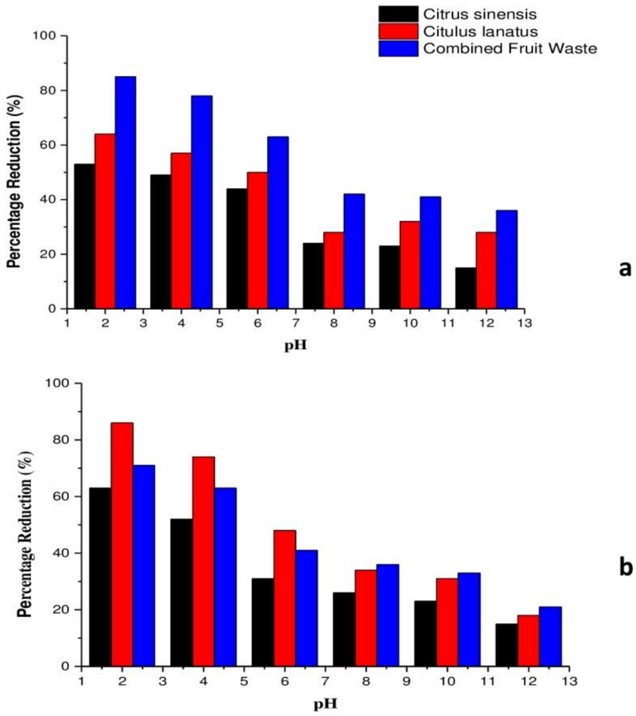

Figure 3. *Effect of pH on Adsorption Process (a) Cr^{3+} (b) Pb^{2+}*

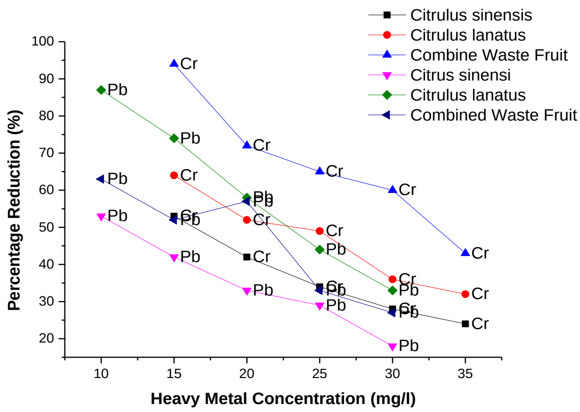

Figure 4. *Effect of Cr^{3+} and Pb^{2+} on Absorption efficiency*

Desorption Study

All the solution used for the desorption process recorded a high recovery of Cr^{3+} and Pb^{2+} from the biosorbent and are also non-polluting and non-damaging. This research is in agreement with the research available in literature (Zhang et al., 2018; Yang and Cui, 2013). This high efficiency recovery supports the fact that exchange ion depends on desorption. The recovered absorbents (*Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combine waste rind) still show high Cr^{3+} and Pb^{2+} removal even after triplicating the process indicating its high reuses capacity for commercial application (*Figure 5*).

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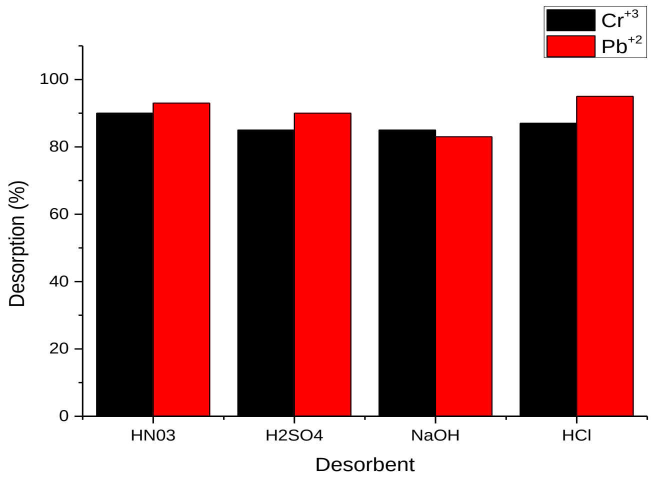

Figure 5. *Desorption Effeciency of Different Pollutants for the Desorption of Pb^{2+} and Cr^{3+}*

Comparison of the Removal Efficiency of Combined Fruit Waste and Other Biosorbents

Comparative study of the removal efficiency of the combination of *Citrus sinensis* peel and *Citrulus lanatus* rind with and other Biosorbents shows high removal efficiency by the combination of *Citrus sinensis* peel and *Citrulus lanatus* rind (*Table 1*). The difference in uptake by the Biosorbents could be attributed to difference in surface area, binding sites and experimental conditions.

Table 1. *Comparative Biosorption of Cr^{3+} and Pb^{2+} by Different Agricultural Waste*

SN	Biosorbent	Heavy Metal	Percentage Reduction (%)	References
1	*Citrus sinensis*	Cr^{+3} and Pb^{+2}	53, 63 (pH 2)	Present Study
2	*Citrulus lanatus*	Cr^{+3} and Pb^{+2}	64, 86 (pH 2)	Present Study
3	Combination of *Citrus sinensis and Citrulus lanatus*	Cr^{+3} and Pb^{+2}	85, 71 (pH 2)	Present Study
4	Eggshell	Cr^{+3}	99 (pH 7.2)	Park et al., 2007
5	*Citrus tangerine, Actinidia deliciosa, Musa acuminate* (waste)	Cr^{3+}	88, 91, 42	Al-Qahtani, 2016
6	*Brassica napus*	Pb^{+2}	94	Morosanu et al., 2017
7	*Saccharum officinarum* bagasse	Cr^{3+}	94	Rico et al., 2018
8	*Glycine max*	Pb^{+2}	79 (pH 4)	Gaur et al., 2018
9	*Saphora japonica* pod	Pb^{+2}	59 (pH 6)	Amer et al., 2015

Adsorption Isotherms

Langmuirs and *Freundlich* isotherms for Cr^{3+} and Pb^{2+} is approximately 1 signify the suitability of *Langmuir* and *Freundlich* isotherms in indicating equilibrium sorption (*Table 2*). The separation factor (Z) for *Langmuir* isotherms was found to be between the ranges of 0-2 signifying that the adsorption of Cr^{3+} and Pb^{2+} by the surfaces of the peels were favourable (Mallampati et al., 2015).

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Table 2. *Isotherm Parameters for Adsorption of (a) Cr^{3+} (b) Pb^{2+}*

a,	Langmuir				Freundlich		
SN	**Fruit Waste**	**q_f (mg/g)**	**b_i (l/mg)**	**R^2**	**K_f**	**n**	**R^2**
1	*Citrus sinensis*	4.35	0.15	0.9557	0.5677	3.8878	0.9349
2	*Citrulus lanatus*	5.06	0.21	0.9756	0.8455	3.4588	0.9436
3	*Combine Fruit Peel*	5.35	0.29	0.9945	1.8873	5.5633	0.9971
b,	**Langmuir**				**Freundlich**		
SN	**Fruit Waste**	**q_f (mg/g)**	**b_i (l/mg)**	**R^2**	**K_f**	**n**	**R^2**
1	*Citrus sinensis*	3.17	0.15	0.9548	1.3878	3.4536	0.9677
2	*Citrulus lanatus*	4.04	0.24	0.9968	3.456	4.4565	0.9998
3	*Combine Fruit Peel*	3.27	0.17	0.9564	1.5733	3.4567	0.9456

Adsorption Kinetics

The correlation coefficient value (r) obtained follow pseudo-second order kinetics model and pseudo-first order kinetic model indicating that absorption occurs due to chemical and physical reaction between the surface of *Citrus sinensis* waste peel, *Citrulus lanatus* waste rind and combines wastes and Cr^{3+} and Pb^{2+} (Elhafez et al., 2017; Salmani et al., 2017; Xu et al., 2013). Since the adsorption of Cr^{3+} and Pb^{2+} by the waste fruit favour second order model, it signifies that the valence electron of the heavy metal binded with the negative charged surface site of the waste fruit in order to attain equilibrium (Elhafez et al., 2017) (*Table 3*).

Table 3. *Kinetics Parameters for Adsorption of (a) Cr^{3+} (b) Pb^{2+}*

a,	Pseudo-Second Order Parameter				Pseudo-First Order Parameter		
SN	**Fruit Waste**	**K_2 (g mg^{-1} min^{-1})**	**q_i (mg/g)**	**R^2**	**K_1 (min^{-1})**	**q_i (mg/g)**	**R^2**
1	*Citrus sinensis*	0.1678	5.74	0.9923	0.1878	5.74	0.8701
2	*Citrulus lanatus*	0.2558	7.26	0.9776	0.2434	7.26	0.9433
3	*Combine Fruit Peel*	0.3455	7.78	0.9996	0.3558	7.78	0.9572
b,	**Pseudo-Second Order Parameter**				**Pseudo-First Order Parameter**		
SN	**Fruit Waste**	**K_2 (g mg^{-1} min^{-1})**	**q_i (mg/g)**	**R^2**	**K_1 (min^{-1})**	**q_i (mg/g)**	**R^2**
1	*Citrus sinensis*	0.216	3.60	0.8751	0.2763	3.60	0.8350
2	*Citrulus lanatus*	0.278	4.64	0.9973	0.3747	4.64	0.9387
3	*Combine Fruit Peel*	0.235	3.74	0.9278	0.3543	3.74	0.8756

Conclusion

Based on the findings of the current work, it could be concluded that *Citrus sinensis* peel and *Citrulus lanatus* rind as well as combination of the two fruit wastes can be used to reduce or control heavy metals from industrial effluent. Although, *Citrulus lanatus* is best for Pb^{2+} removal while combination of the two fruit wastes is best in Cr^{3+} removal. Further investigations involving the use of the agricultural wastes could lead to the discovery of more effective materials or compound materials for control of heavy metal pollutants in waste waters. Further research is needed on how to strengthen the uptake efficiency by such natural materials (the combination of *Citrus sinensis* peel and *Citrulus lanatus* rind) so as to enhance their effectiveness.

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