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FRUIT AND AGRICULTURAL WASTE CORTEX AS NATURAL RESINS ADSORBENTS FOR REMOVAL OF HEAVY METAL IONS FROM WASTE WATER

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Abstract

Agricultural waste peels, may act as cost effective and efficient adsorbents for the removal of heavy metals contaminates from waste water. raw peels of orange (*Citrus sinensis*), lemon (*Citrus limon*), bitter orange (*Citrus aurantium*), broad bean (*Vicia faba*), pumpkin (*Cucurbita pepo*) and squash (*Cocozzelle)* biomass, have been used as a biosorbent for metal ion removal from synthetic waste aqueous solution by batch process. Fourier transforms infrared (FTIR) spectroscopy and scanning electron microscope techniques were used to characterize the Agricultural peels. The (FTIR) spectra showed that the intensities of functional groups after binding with metal ions were slightly reduced and also the peak positions were undergoes red shift. It had been found that the biosorption capacities were significantly affected by solution PH, contact time and particle size of peels. The best removal efficiency for Pb(II) was achieved by squash, while the higher removal efficiency for Cd(II) and Cu(II)was obtained by bitter orange and lemon respectively.

***Keywords*:** Agriculture peel waste, Biosorption, Heavy metals, Binding capacity, Metal ion uptake

Introduction

Heavy metal pollution has become one of the most serious a chronic environmental problems. They can be released into the aqueous environment from a variety of sources such as rocks and metalliferous minerals, but mainly anthropogenic inputs from agriculture, metallurgy, energy production, microelectronics, mining, sewage sludge and waste disposal, effluents from the plastic, textile industry (Pesantes *et al.*, 2019; Landa, 2005; Shen *et al.*, 2019; Abdel-Raouf and Abdul-Raheim, 2017; Valdman *et al.,* 2001). They are the main hazardous non-degradable substances, persistence and can be accumulate in the environment elements such as food chain, thus may pose a significant danger to human health (Bempah and Ewusi, 2016; Khan *et al.*, 2013). Research interest into the production of cheaper adsorbents to replace costly wastewater treatment methods such as chemical precipitation, ion-exchange, electroflotation, membrane separation, reverse osmosis, electrodialysis, solvent extraction, etc. (Azizi *et al.,* 2016; Victor-Ortega *et al.,* 2016; Gunatilake, 2015; Selatnia *et al.*, 2004; Makanyire *et al.*, 2016) are attracting attention of scientists. The major shortcomings of the conventional treatment include high capital investment, low efficiency, production of toxic sludges and economical unfeasibility for small-scale industries (Ahmad *et al*, 2016; Barakat, 2011). These disadvantages, together with the need for a more economical and effective method for recovery of metal from wastewater, have led to the development of alternative separation technologies. Many studies have already been done on the biosorption ability of agricultural waste materials such as palm and coconut fibers (Iqbal and Saeed, 2002), fibrous papaya wood networks(Saeed *et al.,* 2005), crab shells(Vijayaraghavan *et al.,* 2006) and even coconut shell powder (Pino *et al.,* 2006).

The native exchange capacity and general sorptive characteristics of these materials derive from their constituents polymers. Cellulose, lignin, pictins and hemicellulose (Laszlo, 1996; Nada and Hassan, 2003). The efficiency of agricultural residues can be enhanced by chemical modification (Zhang *et al.*, 2013; Nada and El-Wakeel, 2006). Studies of the adsorption of metal ions such as Ni(II), Pb(II), Cu(II) and Co(II) using orange peel modified with nitric acid have already been done (Annadurai *et al.*, 2002; Ajmal *et al.*, 2000). The effectiveness of the adsorbents depends to a large extent on their chemical composition particularly on functional groups. Carboxyl groups and hydroxyl groups can play a vital role in metal ions adsorption (Davis *et al.*, 2003; Lakshmipathy *et al.*, 2015). The aim of this work was to demonstrate the use of waste materials from different agricultural peels like orange (*Citrus sinensis*), lemon (*Citrus limon*), bitter orange (*Citrus aurantium*), broad bean (*Vicia faba*), pumpkin (*Cucurbita pepo*) and squash (*Cocozzelle*), as an excellent source of biomass for the chelating of heavy metals and its applications to eliminate these contaminants from wastewater.

Material and Methods

Reagents

All reagents were obtained from Merck Germany as analytical grade and were used as received without any further purification procedure.

Analytical Methods

(i) Determination of metals concentration

A standard stock solution (1000 mg/l) of Cu(II), Cd(II), Pb (II) ions were prepared by dissolving of metal salts of $Cu(NO_3)_2.3H_2O$, $Cd(NO_3)_2$ $.4H_2O$, and $Pb(NO_3)_2$ in de-ionized water. Several concentrations (5-25) mg/ l of Cu (II), Cd (II), and Pb (II) ions were prepared from standard stock. The absorbance of these solutions were measured at the specified wavelength (λ max) 324.8 nm for Cu, 228.8 nm for Cd, and 283.3 nm for Pb. The concentrations of metals in all samples were determined using atomic absorption spectrometer (Phonex-986). Precision of the metal measurement was determined by analyzing (in triplicate) the metal.

(ii) Characterization technique

Samples of some original peels, before and after metal binding were confirmed by a FTIR spectrometer (Fourier Transform Infrared Spectroscopy ABB/spectrolab MB3000). The samples were ground well to make KBr pellets under hydraulic pressure of 400 kg/cm^2 and spectra were recorded in the range of 400-4000 cm^{-1}. In each scan, the amounts of the sample and KBr were kept constant in order to know the changes in the intensities of characteristic peaks with respect to the structural changes. The PH was determined using Hanna instrument PH$_2$ll Microprocessor PH Meter. The adsorbents were subjected to Scanning electron microscope (SEM). The SEM was carried out on an SEM TESCAN vegalll Czech Republic.

(iii) Biomass preparation

The different cortexes orange (*Citrus sinensis*), lemon (*Citrus limon*), bitter orange (*Citrus aurantium*), broad bean (*Vicia faba*), pumpkin (*Cucurbita pepo*) and squash (*Cocozzelle*), were washed with tap water (more than 4 times to remove any adhering dirt), then rinsed with double-deionized water and dried in the sun light for 6 days, then the different materials were dried in an oven at 70 ^{o}C for four hours until reached a constant weight. Once dried, cortexes were milled into powder before its use in the biosorption experiments. Dried biosorbents were stocked in desiccator at a room temperature of 30 ^{o}C.

(iv) Experimental work

The adsorption of metal ions from the aqueous solutions was studied. One gram biosorbent was introduced to 100 ml of synthetic wastewater solution at different PH (2.0, 5.0 and 8.0 ± 0.1). The reaction mixture was agitated at 125 rpm on a shaker. Agitation contact time was kept to 1, 2 and 4 h to estimate the removal efficiency. All samples were filtered through Whatman filter paper (No. 42) and the metal ions concentration was determined in the filtrate. The whole experiment was conducted in a laboratory at a constant room temperature of 30 ^{o}C. Metal concentration measurements during the experimental assessments were performed by atomic absorption spectrophotometer (AAS) (Phonex - 986). The percent removal of metals was calculated using the equation:

$$\%R = (Ci - Cf) \times 100 / Ci$$

where R = metal removal; Ci = initial metal concentration in solution used (mg/L); and Cf = final metal concentration in solution (mg/L).The effect of several parameters, such as, Influence of particle size, pH, and contact time were studied. All the experiments were carried out in triplicate, the percent relative standard deviation for results was calculated and if the value of standard deviation for any sample was greater than 5% the data were not used.

Results and Discussion

Characterization

The infrared spectrum of some of the agricultural waste peels namely pumpkin and *Vicia faba* was taken before and after adsorption of Pb^{+2}, Cu^{+2} respectively. The IR charts reveal the presence of several functional groups on the surface of the biosorbents which are capable of binding metal ions. The spectra are shown in [Figure 1(a-d)]. A broad peak at (3468-3413) cm$^{-1,}$ representing O-H group vibration. Peaks at (2932-2919) cm^{-1} is related to CH- aliphatic stretching vibration, while peaks at (1734- 720) cm^{-1} representing C=O group, Peaks at (1639-1619) cm^{-1} and (1072-1038) cm^{-1} are attributed to N-H and C-O of alcohol respectively (Zhang *et al*, 2013). It was clear from the FT-IR charts that after metal ion binding, the intensities of functional groups were reduced and also the peak positions were undergoes red shift (Ahmad *et al,* 2016; Thirumavalavan *et al,* 2011). Red shift has been observed in the range (8-55) cm^{-1} for the above functional groups, indicating their role in binding metal ions. For pumpkin several shifts were observed in the wave number of functional groups, Figure -1(c). Peak at 3413 cm^{-1} was shifted to 3468 cm^{-1}, 2919 cm^{-1} shifted to 2932 cm^{-1}, peak at 1720 cm^{-1} was shifted to 1734 cm^{-1}. For *Vicia faba* also several shifts were also observed in the wave number of functional groups, Figure -1(d). Peak at 3440 cm^{-1} was shifted to 3456 cm^{-1}, peak at 2920 cm^{-1} shifted to 2928 cm^{-1}, peak at 1632 cm^{-1}, 1056 cm^{-1}, was shifted to1640 cm^{-1}, 1072 cm^{-1}, respectively. In the SEM micrograph, surface morphology of *Vicia faba* peel is shown in (Figure2a). The surface of peel before coordinating with Cu^{+2} (which is taken as an example) is coarse and has pores. However, after adsorption with metal ion, the surface morphology of metal-loaded *Vicia faba* peel (Figure 2b) has been changed which was entirely different from the peel before binding with metal ion, which proves the adsorption of metal ions on the surface of adsorbent.

Influence of particle size in the removal efficiency

In order to determinate the influence of the particle size in the removal efficiency, two different particle sizes of fine powder (1 mm, and 2 mm) were used for fruit cortex in experiments for the removal of metals in solution. Particle size has a great influence on the removal of heavy metal ions (Khairia, 2016). Interesting results were obtained through experimental work. It was found that 1 mm absorbent particle size is more effective in removing heavy metal by about (10-12.5 %) than the 2 mm particle size. so considering this results only 1 mm particle size absorbents were used in this experiment. Regarding the particle size, it was expected that smaller particle size had the highest biosorption effect, because small particles can provide more contact surface. Experimental data agreed with the expected results, the smallest particle size (1 mm) of absorbent produce better results in metals removal than 2 mm particle size. Figures (3-5) show the variation of heavy metal uptake with particle size using 1 gm. bisorbent at pH 5.

Effect of contact time

Contact time is an important parameter in the absorption phenomena. The effect of contact time on absorption process of metal ions from synthetic solution was studied by many authors (Ali *et al.,* 2014; Nawar *et al.,* 2013; Khoiriah *et al.,* 2015). The results indicated that the equilibrium time was dependent on the nature of absorbent and on metal ion concentration. Therefore it's important to study its effect on the capacity of metal uptake. In our study three contact time (1, 2 and 4 hours) were used for the investigation of heavy metal removal from synthetic solution at room temperature. It's evident that's the bio-absorbents used in this study are efficient in removing Pb^{+2}, Cd^{+2}, and Cu^{+2} from synthetic solution in a varying capacity. The effect of contact time on the removal of heavy metal ions is illustrated in figures (6-8). It was found that the removal efficiency was increased by (21-30 %) as the contact time increases. This is in agreement with results obtained in many research articles (Ali *et al.,* 2014; Saifuddin and Kumaran, 2005; Bernard *et al.,* 2013).

Effect of pH

The pH of synthetic waste water has a significant impact on the uptake of the heavy metals (Thakur and Parmer, 2013; Parmar and Thakur, 2013). All experiments were carried out in the PH values of (2, 5 and 8 ± 0.2). The adsorption capacity of Pb^{+2}, Cd^{+2} and Cu^{+2} as a function of PH is shown in figures (9-14). It was observed that the ability of removing heavy metals depends on PH of solution and this depend on the ion state. The highest uptake capacity was investigated at pH 5. At pH 2 the more hydrogen ions competing with metal ions for adsorption sites, thus minimizing their adsorption. At PH 8 the capability of adsorption declined due to precipitation of metals and formation of hydroxide, this is in agreement with results obtained by (Singana, 2011 and Ho, 2005).

Conclusions

The following conclusions can be withdrawn from the present study:

- This work examined the adsorption of Pb^{+2}, Cd^{+2} and Cu^{+2} ions from synthetic solutions using raw orange (*Citrus sinensis*), lemon (*Citrus limon*), bitter orange (*Citrus aurantium*), broad bean (*Vicia faba*), pumpkin (*Cucurbita pepo*) and squash (*Cocozzelle*) peels.
- It was found that 1 mm absorbent particle size is more effective in removing heavy metals by about (10-12.5 %) than the 2 mm particle size.
- The maximum uptake capacity for all peels was found to be four hours contact time, at pH 5
- The adsorption capacity for orange and bitter orange was found to be $Cd^{+2} > Cu^{+2} > Pb^{+2}$. For lemon was $Cu^{+2} > Cd^{+2} > Pb^{+2}$, broad been was $Cu^{+2} > Pb^{+2} > Cd^{+2}$. while for pumpkin and squash was $Pb^{+2} > Cu^{+2} > Cd^{+2}$.
- The (FTIR) spectra showed that the intensities of functional groups after binding with metal ions were slightly reduced and shifted towered higher wave number.

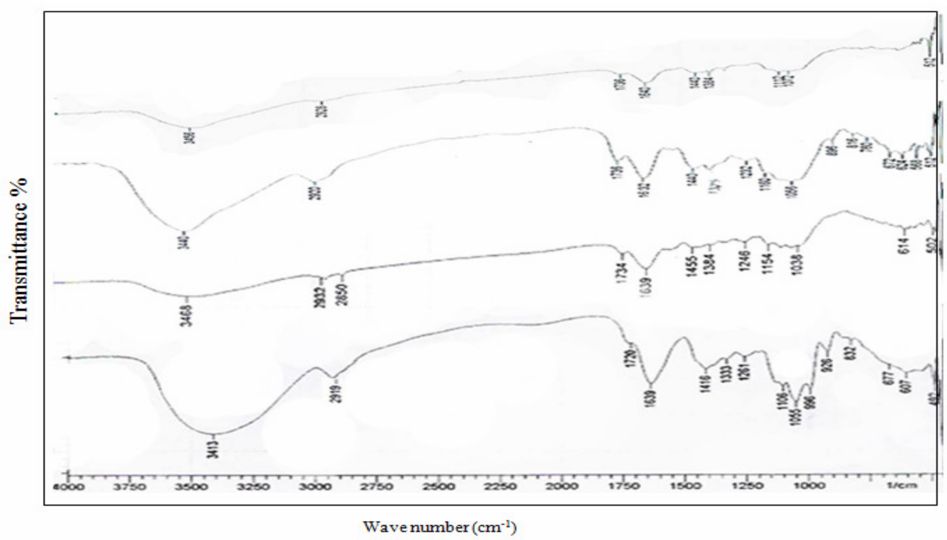

Fig. 1 : FT-IR spectra of (a) pumpkin raw peel, (b) pumpkin peel binded with Pb^{+2}, (c) *Vicia faba* raw peel,(d) *Vicia faba* peel with Cu^{+2}

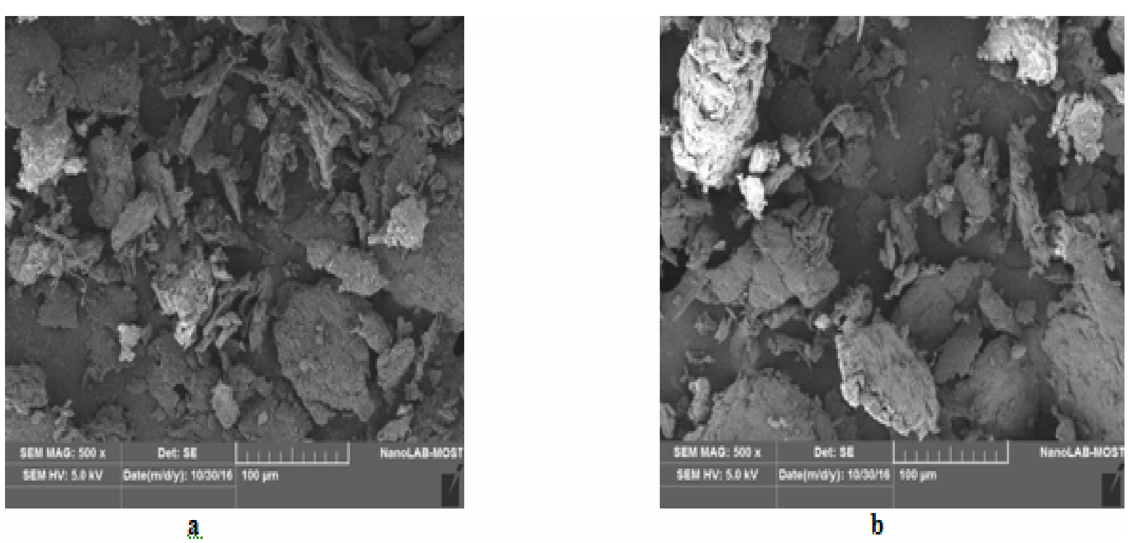

Fig. 2 : SEM images (a) *Vicia faba* peels before binding with metal ion. (b) *Vicia faba* peels after binding with metal ion

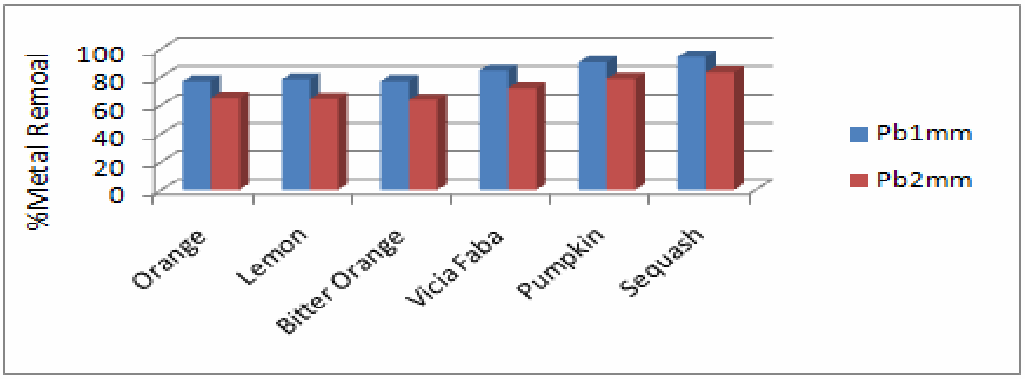

Fig. 3 : Effect of particle size on % removal of lead ions by different waste peels, using four hours contact time and at pH 5.

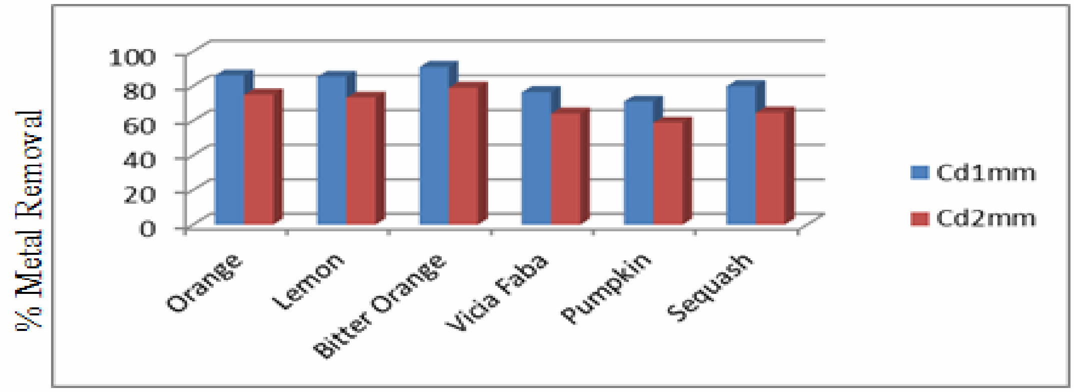

Fig. 4 : Effect of particle size on % removal of cadmium ions by different waste peel using four hours contact time and at pH 5.

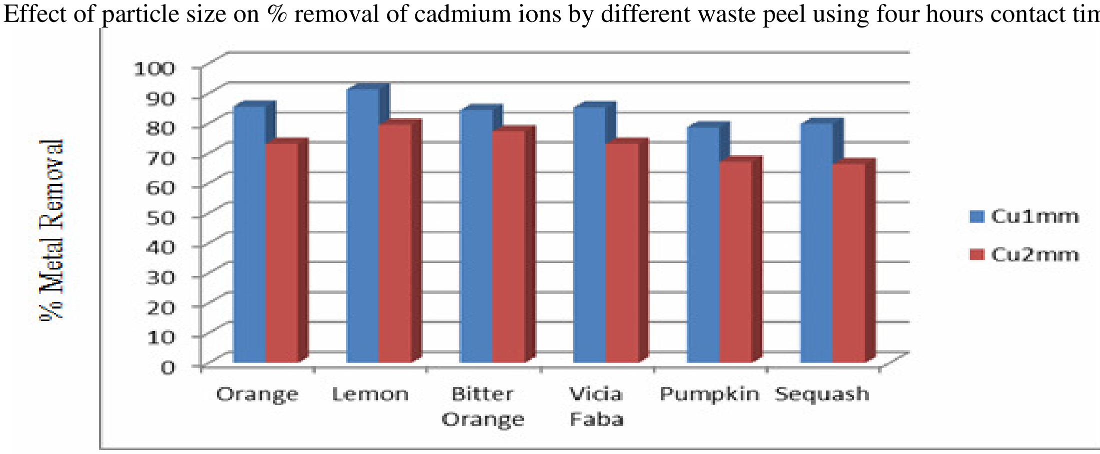

Fig. 5 : Effect of particle size on % removal of copper ions by different waste peels using four hour contact time and at pH 5.

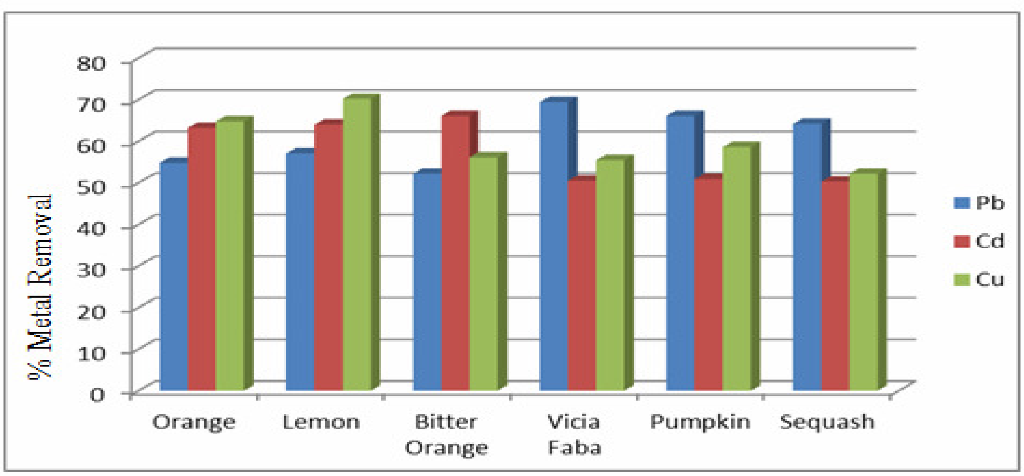

Fig. 6 : Effect of contact time on ions removal using 1mm particle size for 1h at pH 5.

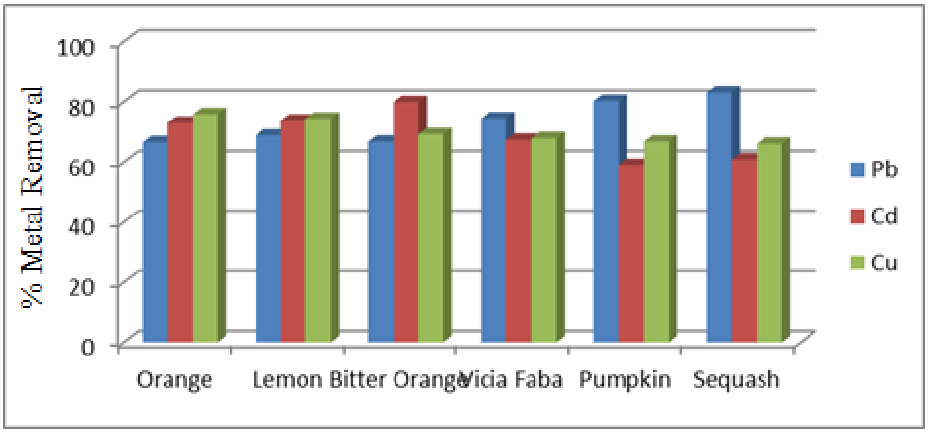

Fig. 7 : Effect of contact time on ions removal using 1mm particle size for 2h at pH 5.

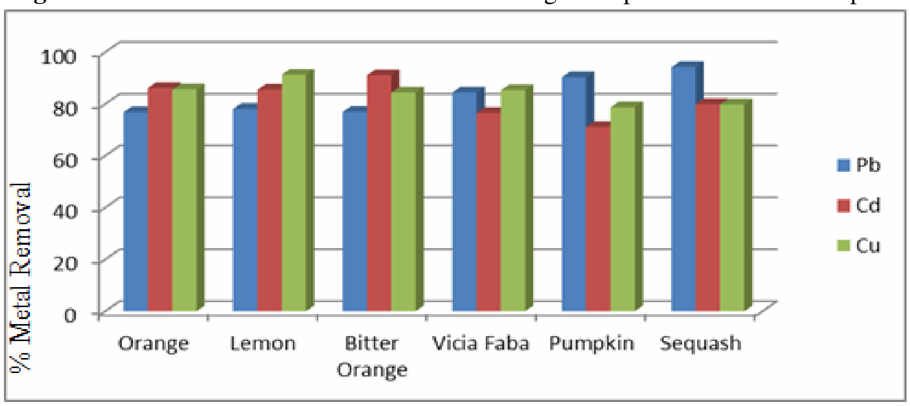

Fig. 8 : Effect of contact time on ions removal using 1 mm particle size for 4h at pH 5.

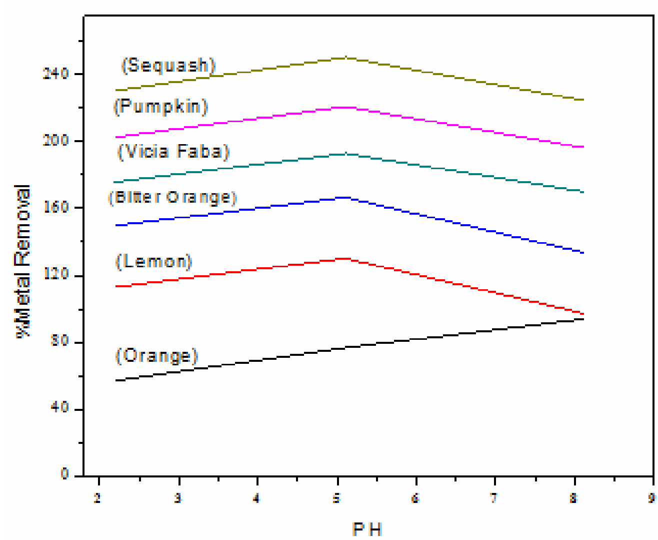

Fig. 9 : Effect of pH on removal percentage of Pb^{+2} , Cd^{+2} and Cu^{+2} ions using 1mm particle size orange cortex and 4 hours contact time

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