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Efficacy of Adsorption of Cu (II), Pb (II) and Cd (II) Ions onto Acid Activated Watermelon Peels Biomass from Water

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Abstract: ***The efficacy of the watermelon peel biomass was tested for the removal of lead, copper and cadmium metal ions using batch experiments. Watermelon peel was first modified by exposing it to1N sulphuric acid. The effect of the treatment on morphological characteristics of the adsorbent was evaluated by mid infrared spectroscopy (MIR) and Scanning Electron Microscopy (SEM). The levels of adsorption of Cu^{2+}, Pb^{2+} and Cd^{2+} on unmodified watermelon peel (UMWP) and modified watermelon peel (MWP) was studied by varying parameters like pH, dosage, initial concentration of the metal ions and time. Equilibrium was described by Langmuir equation with the maximum adsorption capacities for Cu^{2+}, Pb^{2+} and Cd^{2+} of 134.23 mg/g, 130.23 mg/g and 97.149 mg/g, respectively. Time-course measurements indicated involvement of pseudo-second-order kinetics in adsorptions. Desorption efficiencies of 94.98 % Pb^{2+}ions, 99.79 % in Cu^{2+} and 99.23 % Cd^{2+} in chemically modified watermelon peels were recorded.***

Keywords: Watermelon peel; chemical modification; adsorption efficiency; metal ions; desorption efficiency.

1. Introduction

Pollution of water sources due to disposal of toxic heavy metals such as copper, zinc, nickel, cadmium and lead, among others, has been of great concern over the last few decades (Liang *et al.,* 2012). Unlike organic wastes, heavy metals are non-biodegradable and they can accumulate in living tissues, causing various diseases and disorders such as cancer, nervous system damage and ultimately death (Rasheed *et al.,* 2013). Therefore, they need to be removed before discharge (Liang *et al.,* 2011). Climate change and industrialization have made it difficult to provide sufficient clean water for domestic use. Currently, there is a need to come up with simple and affordable methods of cleaning polluted water. This is especially important in developing countries where people depend on river water which can be highly polluted.

Decontamination of toxic pollutants from water poses a major challenge, and therefore numerous approaches have been explored for their removal (Jaramillo *et al.,* 2009). Biosorption has shown promising results in removal of toxic ions from water (Babel and Kurniawan, 2003). The adsorption properties of for carbonized samples biological waste materials, such as those derived from peat, wood, pine bark, and leaves, among others, have been mainly reported (Pino *et al.*, 2006). However, activated carbon, is not affordable, and therefore, there is need for alternative cheaper products (Babel and Kurniawan, 2003). Natural sorbents, mainly obtained from plant wastes and fruit peels, have been found effective in removing metal ions from waste water without chemical modifications (Hossain *et al.,* 2012a).

Modified sorbents derived from locally available materials such as fruit wastes have received increasing attention for removal and recovery of heavy metals from wastewater systems (Moyo and Chikazaza, 2013). Fruits wastes are inexhaustible, non-edible and renewable polymeric materials which are discarded as wastes (Moyo and Chikazaza, 2013). This study sought to assess the kinetics and efficiency of watermelon peel in their natural and modified form for adsorption of Cu, Pb and Cd. To shed light on the structural modification of the watermelon peel, their surface morphologies and features were assessed using scanning electron microscopy (SEM) using mid-infrared spectroscopy (MIR).

2. Materials and Methods

2.1 Adsorbent preparation

2.1.1 Natural sorbents

The watermelon peels were collected locally and were transported to the laboratories, washed thoroughly with deionized water to remove impurities, then cut into small pieces and dried in an oven at 105 ºC to eliminate moisture. The dried adsorbents were crushed and sieved. The resulting solids were labeled and kept in desiccators until used.

2.1.2 Chemical modification of the adsorbents

Each crude adsorbent was mixed with 1N sulphuric acid solution a ratio of 1:2 (Weight:Volume), and thermo-chemically treated at a temperature of 150 ºC for 24 hours. Each product was then washed with distilled water to remove the excess acid, filtered and kept in sodium bicarbonate solution $NaHCO_3$ (1 %) overnight to eliminate the acid residue (Khalfaoui and Menai, 2012; Moyo and Chikazaza, 2013). Finally, each treated adsorbent was dried at 105 ºC to a constant weight.

2.2 Surface characterization

Functional groups present in the untreated and acid-treated watermelon peels were characterized by MIR spectra obtained by SHIMADZU FTIR 8400S (Kyoto, Japan) spectrometer. The spectra of adsorbents were measured within the range of 600–4000 cm^{-1}. The surface morphologies of the natural and acid modified watermelon peels forms were determined using Scanning Electron Microscope (SEM) (Hossain *et al.,* 2012a). SEM analysis was carried out by the Carl Zeiss- Model EVO 50 equipped with a large field detector and an energy dispersive micro-analysis system (HV- 20.0KV, Detection-Large Field Detector (LFD), Magnification – x800, Working Distance (WD)- 9.3mm, Pressure- 0.98 Torr, Spot – 7.0 and Aperture-1000µm).

2.3 Preparation of stock solutions

Stock solutions of Cu^{2+}, Pb^{2+} and Cd^{2+} ions were prepared from their corresponding metal nitrates. The progressive dilution procedure of the stock solutions was done to get working solutions. The pH of the working solutions was adjusted to the required value with 0.1 M NaOH or 0.1 M HCl.

2.4 Batch adsorption experiments

Each of the weighed amounts of (i) natural watermelon peels (ii) acid treated watermelon were introduced into stoppard reagent bottles containing various concentrations of 50 mL aqueous solutions of Cu^{2+}, Pb^{2+} and Cd^{2+} ions. The suspensions were shaken at room temperature (25°C ± 1°C) using a mechanical agitator for a prescribed time at 160 rpm. The solutions were the filtered through Whatman 42 filter paper and the residual concentration of metal ion was determined by AAS method. The effects of initial concentration (10 - 500 mg/L), contact time (5 - 1440 min), solution pH (2 - 14) and adsorption dose (0.01 - 0.5 g) were evaluated. Optimum conditions were maintained in subsequent experiments. The percentage of removed Cu^{2+}, Pb^{2+} and Cd^{2+} ions (*R*%) in solution was calculated by using Equation 1.

$$R\% = \frac{(C_i - C_o)100}{C_i} \qquad (1)$$

Where, *Ci* and *Co* are the initial and equilibrium metal concentration The amount of metal adsorbed by natural and acid treated watermelon was calculated using Equation 2.

$$q_e = \frac{(C_i - C_e)V}{M} \qquad (2)$$

where, q_e is the metal uptake (mg metal adsorbed per *g* adsorbent), *Ci* and *Ce* are the initial and equilibrium metal concentration, V is the volume of the reaction mixture and M is the mass of dried adsorbent used (Moyo and Chikazaza, 2013).

2.5 Desorption Studies

Desorption and reuse experiments were done to determine desorption ratio and reusability of raw materials. These experiments were carried out as described by Liang *et al*. (2012) and (Hossain *et al*., 2012a). Desorption studies were conducted using 2g of acid treated watermelon peels using each of the following eluents, 0.1 mol/l NaOH, 0.1 mol/L HCL, 0.1 mol/L H_2SO_4, 0.1 mol/L HNO_3, 0.1 mol/L CH_3COOH, tap water and distilled water. The 2 g of the acid treated watermelon peels were placed in 100 mL of (10-100 µg/mL) Cu^{2+}, Pb^{2+} and Cd^{2+} ions, and the mixtures were shaken in rotator for three hours. The solutions were filtered and the amount of metal adsorbed was determined. After adsorption, the metal-loaded gels were filtered, weighed and placed in contact with 50 mL of 0.1 mol/L NaOH and shaken for (10-180) minutes, then the metal ion concentration was determined. Same process was repeated with 0.1 mol/L HCL, 0.1mol/L H_2SO_4, 0.1 mol/L HNO_3, 0.1mol/L CH_3COOH, tap water and distilled water. The regenerated material was washed three times in distilled water and the metal ion added again for another adsorption-desorption cycle. This was repeated five times using the best eluent.

2.6 Adsorption isotherms

To characterize the biosorption for unmodified and acid modified watermelon peels, Langmuir and Freundlich models were used. The Langmuir model makes assumptions such as monolayer adsorption and constant adsorption energy while the Freundlich model deals with heterogeneous adsorption. Langmuir equation of adsorption isotherm is;

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{b\,q_{\max}}\right)\frac{1}{C_e}, \qquad (3)$$

Where, $q_{\max}$ and b are the Langmuir constants. A plot of $1/q_e$ versus $1/C_e$ gives a straight line with $1/q_{\max}$ as the intercept and $1/bq_{\max}$ as the slope, and hence $q_{\max}$ and b can be calculated.

The Freundlich equation of adsorption isotherm is;

$$In\,q_e = InK_F + \frac{1}{n} InC_e, \qquad (4)$$

Where, q_e is the maximum amount of adsorption (mg/g), K_F the constant representing the adsorption capacity, and *n* is the constant depicting the adsorption intensity. A plot of *In* q_e versus *In* C_e gives a straight line, and K_F and *n* can be calculated from the intercept and slope, respectively (Moyo and Chikazaza, 2013).

2.7 Adsorption Kinetics

In order to evaluate the kinetic parameters, pseudo-first order and pseudo-second-order models were tested to analyze the adsorption kinetics. The pseudo-first-order equation is expressed as:

$$\log(q_e - q_t) = \log q_e - \left(K_1 t / 2.303\right) \qquad (5)$$

The pseudo-first-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \qquad (6)$$

Where, q_e is the mass of metal adsorbed at equilibrium (mg/g), q_t is the mass of metal at time t (min), K_1 the first-order reaction rate constant of adsorption (min^{-1}), and K_2 the pseudo-second-order rate constant of adsorption (mg/g).The values of K_1 and qe were calculated from the slope and intercept of the plot of log (q_e–q_t) versus t while the values of K_2 and q_e were evaluated from the intercept and slope of a plot of t/qt versus t, respectively (Mekonnen *et al*., 2015).

3. Results and Discussion

3.1 Characterization of watermelon peel

3.1.1 Scanning electron microscope (SEM)

The SEM images of powdered watermelon peels before and after H_2SO_4 treatment are shown in Figure 1.

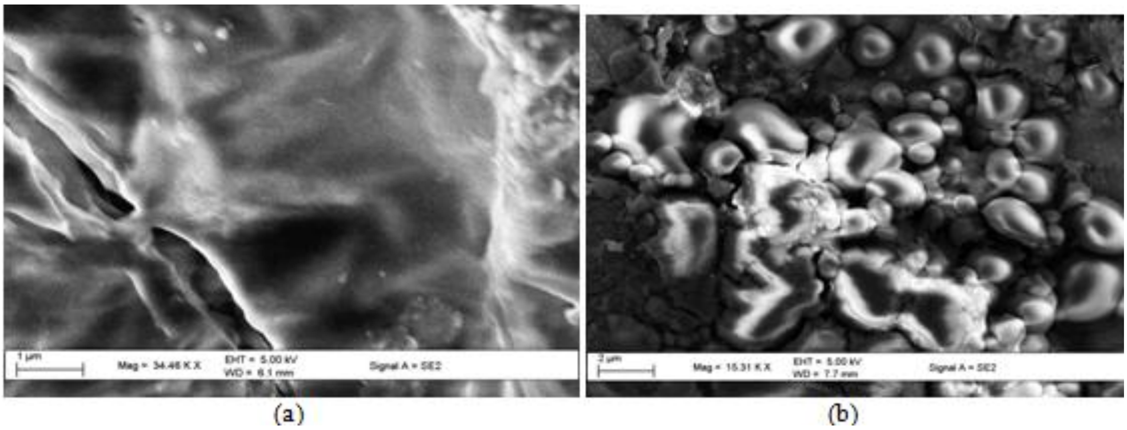


Figure 1: SEM images for unmodified powderd watermelon peels (a) and modified powderd watermelon peels (b).

The SEM images clearly reveal changes in the surface texture and morphology of the watermelon exposed to H_2SO_4. Prior to the treatment, watermelon peels have largely plain surface with few large pores (Figure 1a). However, after H_2SO_4 activation well developed pores appeared on the surface of the watermelon peels (Figure 1b). This suggests increase in surface area, which would result in higher adsorption capacities in the acid modified adsorbents. Similar results were reported on acid activated sawdust, bagasse and sea weed (Kumar *et al*. 2014), in acid modified orange peel (Feng and Guo 2012) and banana peel (Hossain *et al.,* 2012b).

3.1.2 MIR

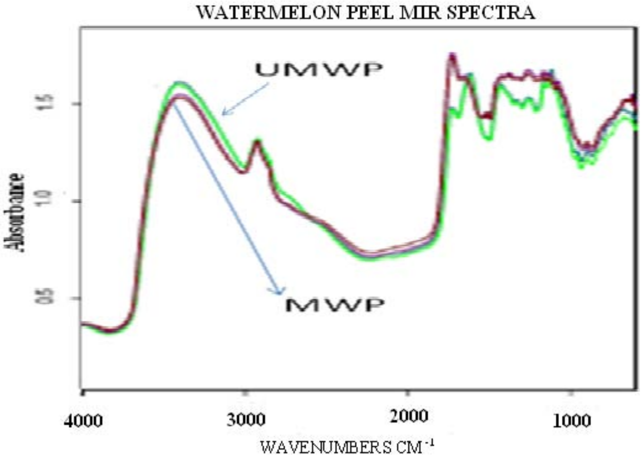
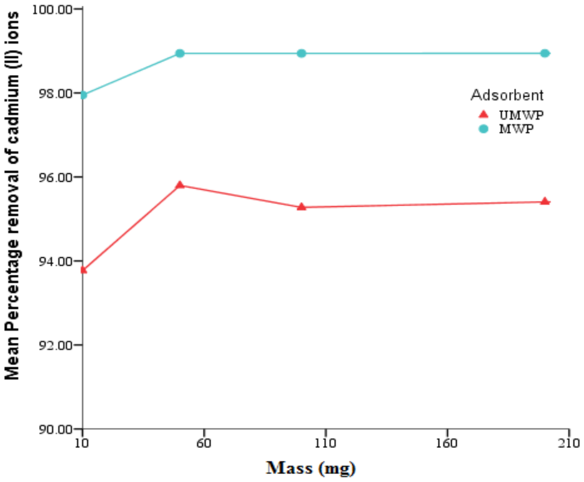


Figure 2: MIR of unmofied (UMW**P)** and modified watermelon peels (MWP)

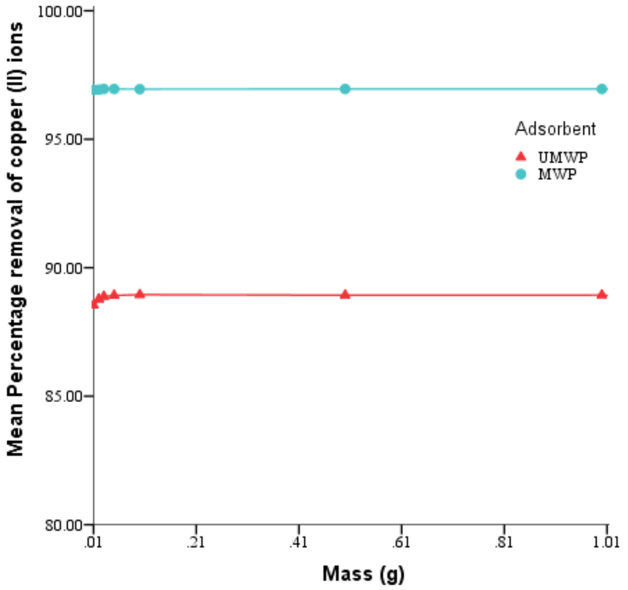
MIR spectra suggest some significant structural changes associated with acid-treatment of watermelon peels. The peaks at 3446 cm^{-1} and 3440 cm^{-1} in untreated and acid-treated watermelon peels respectively correspond to the OH stretching vibrations due to intermolecular and intramolecular hydrogen bonding in polymeric compounds with alcoholic, phenolic and/or carboxylic acid moieties (Liang *et al*., 2011). The peak observed at 2929 cm^{-1} in both UMWP and MWP is assigned to the symmetric and assymetric C-H stretching of aliphatic acids. The difference in absorbance intensities associated with C=O at 1737 cm^{-1} and 1735 cm^{-1} in UMWP and MWP reflects other structural modifications that take place during exposure to the acid. The peak at 1627 cm^{-1} in the UMWP is assigned to conjugated C=O stretching and NH_2 deformation in primary amines. The peak at 1633 cm^{-1} appearing in the MWP may also be indicative of N-H bond of primary amine. At 1440 amd 1438 cm^{-1} peaks in UMWP and MWP show the presence of OH stretch in carboxilic acids. At 1390 cm^{-1} and 1176 cm^{-1} new peaks emerge in the modifed peels which may be assigned to $^{-}SO_2$ symmetrical stretch from sulfonyl chlorides. The peaks at 1272 cm^{-1}, 1278 cm^{-1} and 1106 cm^{-1} are indicative of presence of C-O stretch and C-O-C antisymmetric stretch associated with esters, ethers and lactones.

3.2 Effect of experimental conditions

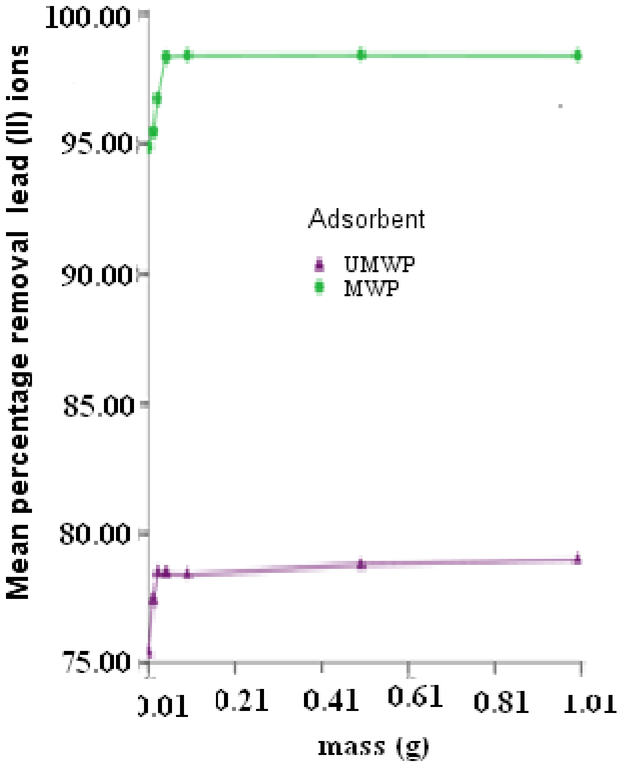
3.2.1 Effect of adsorbent dosage



(a)



b)



c)

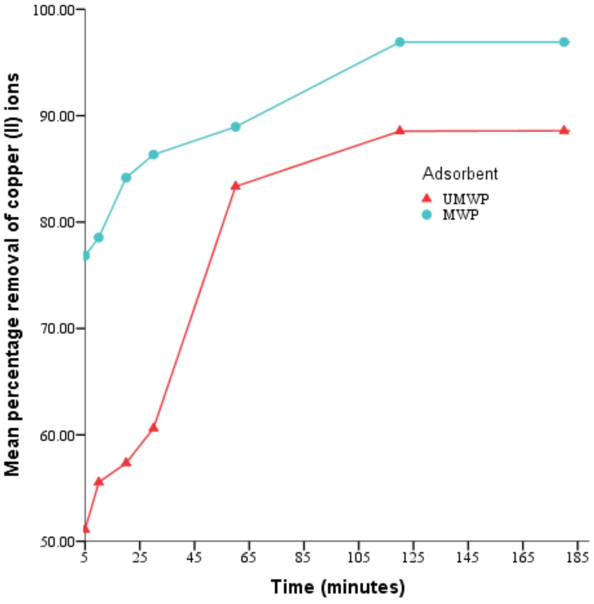
Figure 3: Percentage removal of a) Cd (II), b) Cu(II) and c) Pb (II) ions at different dosages of acid modifed (MWP) and unmodified watermelon peels

Uptake of metal was greatly influenced by adsorbent dosage as shown in Figure 3. Optimum uptake of Cd (II) ions following acid modification of watermelon peels increased from 95.8 % to 98.9 %; that of Cu(II) ions increased from 88.9 % to 97.0 % and that of Pb (II) from 77.9 % to 98.3 % . The high percentage removal of metal ions after acid modification can be attributed to improved surface texture and micro pore structure after acid modification facilitating easier penetration of ions to the adsorption sites (Anwar *et al.*, 2010).

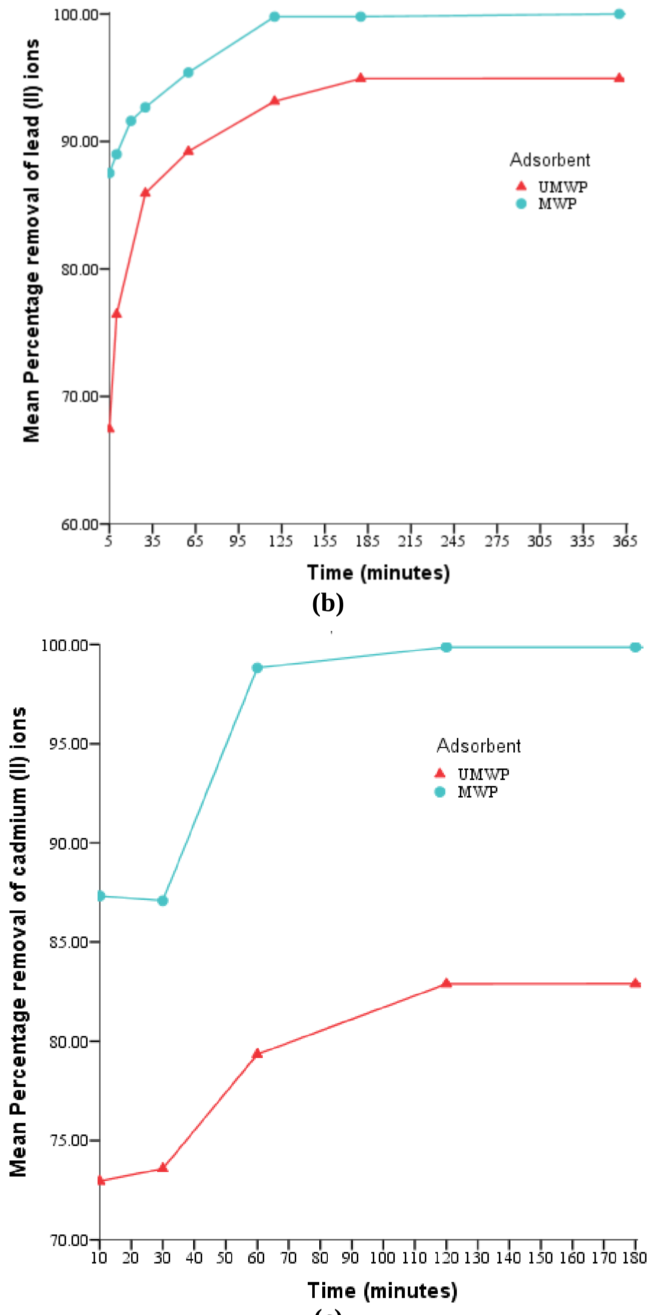
In adsorption experiments with both MWP and UMWP peels metal ions uptake increased with increase in adsorbent dosage to a maximum and thereafter percentage removal the metal ions did not change significantly. This reflects higher availability of active binding sites at higher doses of the adsorbent (Anwar *et al.*, 2010; Karthikeyan *et al.*; 2007; Moyo and Chikazaza., 2013).Highest percentage removal was attained at 50 mg for Cd (II) ions, and 10 mg for Cu(II) and Pb (II) ions. 50g was taken as optimim dosage for the subsequent experiments. These results folow patterns similar to those reported by other researchers with different adorbents (Hossain *et al.*, 2012b, Koel *et al.*, 2012, Moyo and Chikazaza., 2013, Dekhil *et al.*, 2011, Srinivasa and Kesava, 2013). Percentage removal of 92.3 % was reported on acid modified maize tassels (Moyo and Chikazaza., 2013) and 94.8 % on study of banana peel (Muhammad *et al.*, 2011).

3.2.2 Effect of contact time on adsorption

The results presented in Fig. 4 indicate that metal ions uptake is very rapid initially and the equilibrium is reached within 120 mins with MWP with removal efficiences of 97.6%, 100.0 % and 99.8 % for Cu^{2+}, Pb^{2+} and Cd^{2+} respectively. The equilibrium time for the UMWP is 180 minutes with Pb^{2+} ions with maximum revoval of 98.8% and 120 mins for $Cu^{2+}$and Cd^{2+} ions with efficienceis of 86.6% and 83.4 % respectively. After this equilibrium time the rate of metal ion removal approached a steady state. Optmum adsorption time in subsequent experiments was taken to be 120 and 180 minutes for MWP and UNMP respectively for all the metal ions. The trends in Figure 4 can be explained by the fact that initially due to presence of a large number of vacant active binding sites, the adsorption rates were relatively high, and then slowed down and levelled off. As time increased the adsorption sites become limited and the remaining vacant surface sites would be increasingly difficult to be occupied by metal ions due to repulsive effects (Anwar *et al.*, 2010). Results obtained in this study show greater percentage removal of Cu^{2+} ions compared some of those reported by (Bunarjee *et al.*, 2012) Benard and Jimoh, (2013), and (Moyo and Chikazaza, 2013) but lower than those reported by (Castro *et al.*, 2011).



(a)



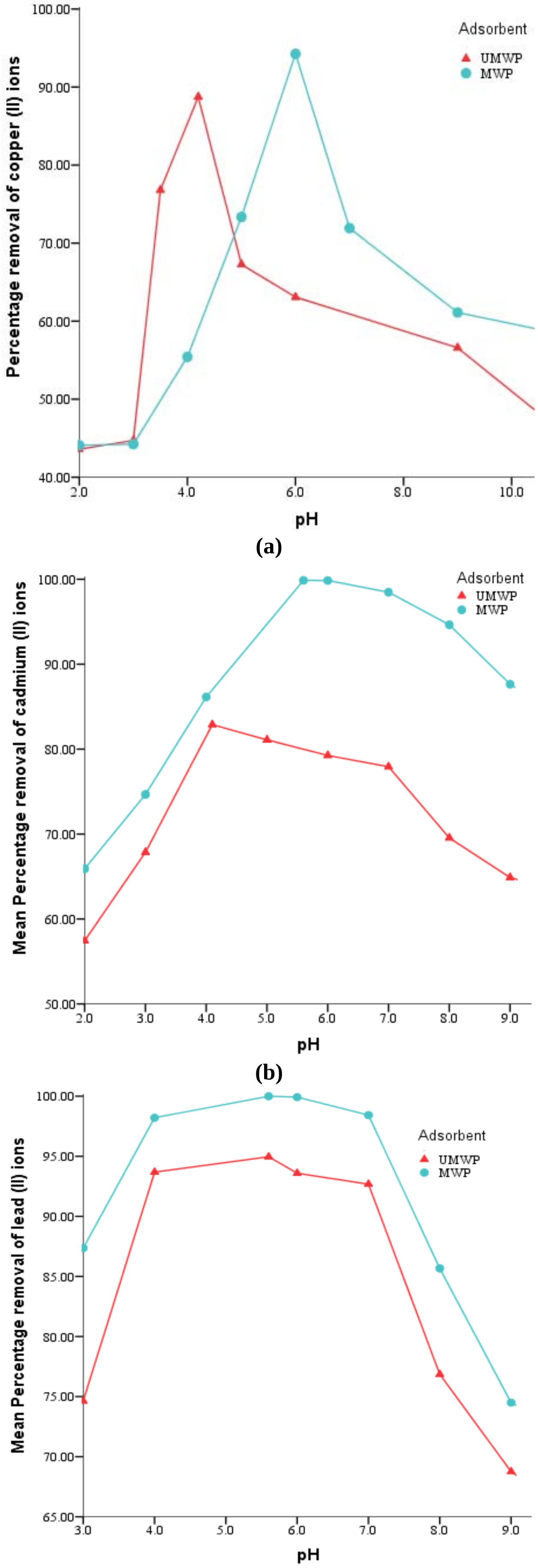
(b)

(c)

Figure 4: Time course % removal of a) Cu(II) b) Pb (II) and Cd (II) (c) ions in acid modifed (MWP) and unmodified watermelon peels (UMWP)

3.2.3 Effect of pH on sorption of metal ions

Results in Figure 5 shows the adsorption behavior of modified watermelon (MWP) and unmodified watermelon peel (UMWP) for Cu^{2+}, $Pb^{2+}$and Cd^{2+} at different equilibrium pH. Maximum adsorption efficiencies with MWP occurred at pH 5.8 (94.3%, 99.9 % and 99.9 % for Cu^{2+}, Pb^{2+} and Cd^{2+}, respectively). For UMWP the optimum pH was 4 (at which 88.7 % , 82.9 % and 95.2 % for Cu^{2+}, Pb^{2+} and Cd^{2+} respectively were adsorbed).



(a)

(b)

(c)

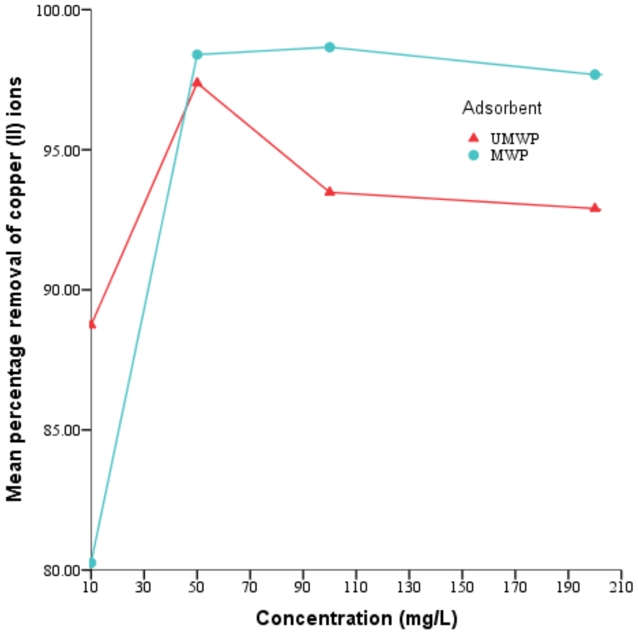
Figure 5: Effect of pH on adsorption efficiency of Cu^{2+}, Cd^{2+} and Pb^{2+} ions

Once optimum pH was reached, further increase in pH resulted in reduction of the amount of metal ion adsorbed. The modified adsorbents had a higher sorption at optimum pH than the unmodified adsorbents. As pH increased, sorption of metal ions increased up to a maximum at pH 5.8 and 6.0 for unmodified and acid modified adsorbents respectively. Beyond pH 6 the percentage removal of metal ions declined.

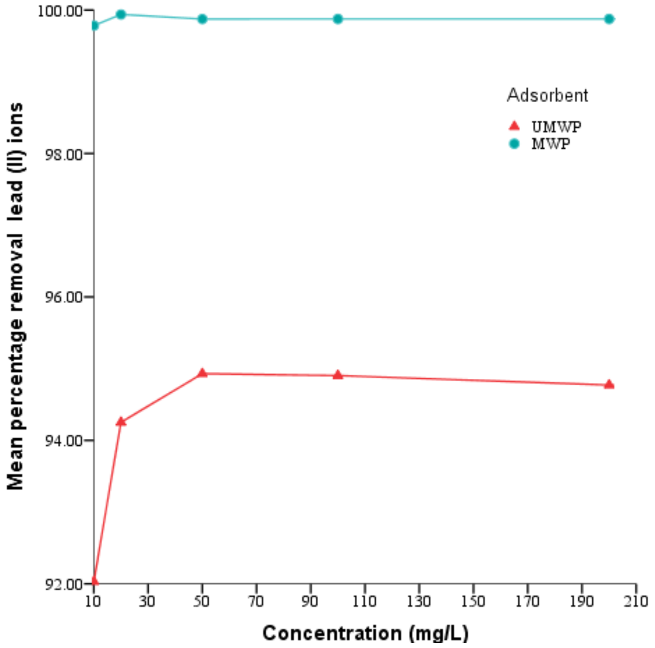
This phenomenon can be explained by the fact that at low pH presence of hydroxonium ions (H_3O^+) which hinders the access of the metal ions to the surface functional groups (Low *et al*., 1995), the carboxyl groups retain their protons reducing the probability of binding to any positively charged ions (Low *et al*., 1995). This may be associated with the presence of carboxyl groups (-COOH). The carboxylate (-COO^-) ligands attract the positively charged ions, binding occurs, indicating that the binding process is likely to be an ion-exchange mechanism that involves an electrostatic interaction between the negatively charged groups in the cell walls and the metallic cations (Moyo and Chikazaza., 2013).

At high pH ^-OH group in the adsorbent and metal ions started precipitating as metal hydroxides (Hossain *et al*., 2012a). Optimum pH was taken to be 5.8 for the MWP and 4 for UMWP in the subsequent experiments. Similar trend was reported in modified maize tassel (Moyo and Chikazaza, 2013, Mwangi *et al.,* 2012).

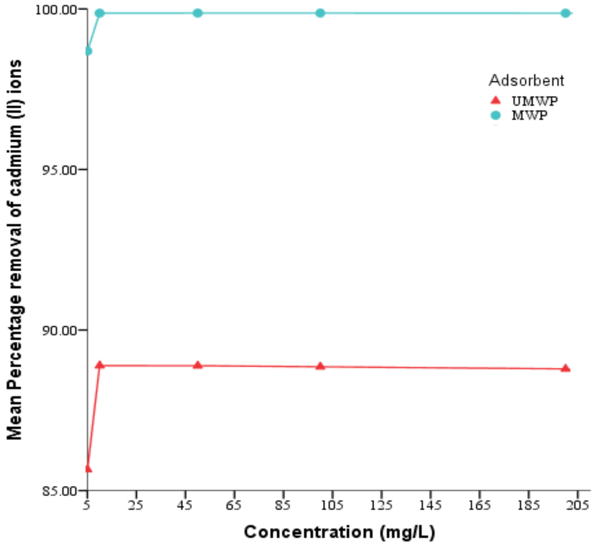
3.2.4 Effect of initial metal ions concentration



a)



b)



c)

Figure 6: Effect of initial concentration on adsorption efficiency of Cu^{2+}, Pb^{2+} and Cd^{2+}

Results in Figure 6 show that sorption of metal ions on unmodified and modified watermelon peels is significantly influenced by the initial concentration of metal ions in aqueous solutions. Percentage removal of metal ions was found to increase with increase in metal concentration to 20 mg/L and 50 mg/L in modified and unmodified watermelon respectively. Maximum percentage removal were 97.3 % and 98.4 % with Cu^{2+} ions, 95 % and 99 % with Pb^{2+} ions and 91.77% and 99.87 % with Cd^{2+} ions in UMWP and MWP respectively. Metal ions uptake increases continuously up to a maximum and thereafter a plateau is observed as the concentration of metal ions is increased.

The observed behaviour may be attributed to the fact that concentration is a driving force for metal ions to occupy available sites (Mwangi *et al.,* 2012, Ilhan *et al*., 2004). At lower concentrations almost all the metal ions were adsorbed very quickly on the outer surface, but further increase in initial concentrations led to fast saturation of the adsorbent and more metal ions were left in solution (Moyo and Chikazaza., 2013: Koel *et al.*, 2012, Arshad *et al.*, 2008). The UMWP had lower percentage removal as compared to the MWP with the three metals ions. These results compare with those reported by (Koel *et al.*, 2012) and (Moyo and Chikazaza., 2013).

3.3 Adsorption Isotherms

Experimental data obtained for Cu^{2+}, Pb^{2+} and Cd^{2+} ions against initial concentration for unmodified and modified watermelon peel (UMWP and MWP) was analysed using Langmuir and Frendlich equation and the results represented in Table 1.

Table 1: Langmuir and Freundlich constants for Cu^{2+}, Pb^{2+} and Cd^{2+} ions adsorption onto MWP and UMWP

Metal ion	Adsorbent	Langmuir			Freundlich		
		Q_{max} (mg/g)	b (L/mg)	R^2	1/n	Kf(mg/g)	R^2
Cu	UMWP	108.498	0.087	0.995	0.845	5.636	0.795
	MWP	134.234	0.028	0.997	0.429	9.977	0.944
Cd	UMWP	28.369	0.023	0.999	1.105	2.183	0.722
	MWP	97.149	0.234	1.000	0.999	18.53	0.993
Pb	UMWP	71.45	0.789	0.999	1.092	14.76	0.991
	MWP	130.23	0.356	0.998	0.93	66.74	0.925

Results in Table 1 indicate that sorption of metal ions with modified and unmodified watermelon peel gave $R^2 > 0.995$ indicating the data fitted well in Langmuir model. This model prescribes a monolayer adsorption and it indicates a chemisorption mechanism (Hossain *et al.,* 2012a, Mwangi *et al.,* 2012, Deng *et al*., 2003). Lower values of b (< 1) were obtained from the all the adsorption processes which indicate the relatively high affinity of the watermelon peel for the metal ions (Hossain *et al.,* 2012a).

Adsorption capacities of 134.234 mg/g, 97.149 mg/g and 130.23 mg/g were recorded Cu^{2+}, Pb^{2+} and Cd^{2+} ions respectively in MWP. Sorption capacites for the metal ioins were higher in acid modified asorbent as compared to theumodified adsorbent. These results compare with those reported in study of watermelon peel (Koel *et al.*, 2012), HCl acid modified mango (Reddy *et al.,* 2012), banana peel (Hossain *et al.*, 2012a) and orange peel (Liang *et al.*, 2012).

3.4 Adsorption kinetic studies

In order to evaluate the kinetic parameters, Pseudo first order and Pseudo second order models were tested to analyse the adsorption kinetics for metal ions on the MWP and UMWP and results recorded in Table 2.

Table 2: Kinetic parameters for asorption of Cu^{2+}, Pb^{2+} and Cd^{2+} ions onto MWP and UMWP

Ion	Adsorbent	Pseudo- First- Order			Pseudo- Second- Order		
		q_e	K_1(mg/g/min)	R^2	q_e	K_2(mg/g/min)	R^2
Cd	UMWP	0.114	0.009	0.199	25.000	$1.552x10^{-4}$	1.000
	MWP	1.622	0.002	0.128	30.303	$6.32x10^{-5}$	0.999
Cu	UMWP	5.559	$2.073 X10^{-2}$	0.595	27.027	$4.907 x10^{-3}$	0.999
	MWP	3.899	$4.61 X10^{-3}$	0.662	29.412	$1.145 x10^{-2}$	1.000
Pb	UMWP	0.571	3.698	0.021	28.571	$2.50 x10^{-2}$	1.000
	MWP	0.471	2.065	0.030	29.412	$3.50 x10^{-2}$	1.000

From R^2, values in Table 2 pseudo second order fits better with the experimental data than pseudo first order model. The R^2 values are >0.999, this shows the suitability of this model. The acid modied forms of the adsorbents recorded the higher values of q_e and K_2 as compared to the raw forms of the adorbents. The model is based on the assumption that chemisorption is the rate limiting step (Bernard and Jimoh, 2013, Mekonnen *et al*., 2015).

3.5 Regeneration of used adsorbents

The regeneration of used adsorbents is crucial for resuse of adsorbents and recovery of valuable metals and for reduction of operation cost for an type of treatment. Regeneration studies (Cu^{2+}, Pb^{2+} and Cd^{2+} ions) were carried out on acid modified watermelon peels using seven eluents and results are presented in Table 3.

Table 3: Desorption of Cu^{2+}, Pb^{2+} and Cd^{2+} ions from acid modified watermelon peels (MWP)

ELLUENT	*Cadmium*	*Lead*	*Copper*
Tap water	$20.02±0.01^a$	$20.17±0.00^b$	$21.42±0.00^a$
Distilled water	$35.92±0.00^d$	$24.44±0.00^d$	$42.34±0.00^d$
0.1M Sulphuric acid	$99.23±0.00^g$	$75.30±0.00^g$	$99.79±0.00^g$
0.1M HCl	$60.55±0.00^e$	$33.33±0.00^f$	$45.42±0.00^e$
0.1M HNO_3	$64.01±0.00^f$	$25.47±0.00^e$	$58.89±0.00^f$
0.1M CH_3COOH	$32.87±0.00^c$	$20.61±0.00^c$	$38.45±0.00^c$
0.1M NaOH	$25.81±0.00^b$	$11.68±0.03^a$	$22.65±0.00^b$
p-value	<0.001	<0.001	<0.001

*Mean values followed with the same small letter within the same column do not differ significantly from one another (one-way ANOVA, SNK-test, $\alpha=0.05$).

The results show that the highest recovery was achieved with 0.1 M sulphuric acid at 95.11%, 75.30 % and 92.97 % for copper, lead and cadmium respectively. Other eluents recorded significantly lower efficiencies ($p < 0.001$). This can be attributed to the fact that in desorption process, H^+ ions replace metal ions (Cu^{2+}, Pb^{2+} and Cd^{2+}) on the surface of watermelon. These results are similar to those recorded in the study involving regeneration of banana peels (Hossain *et al.*, 2012b). The recovery and resuse process was continued upto five times using sulphuric acid as shown in Table 4.

Table 4: Metal (Cu^{2+}, Pb^{2+} and Cd^{2+}) uptake and desorption performance MWP using 0.1M sulphuric acid eluent.

Cycles	**Mean±SE % Adsorption and Desorption**					
	Cu		Cd		Pb	
	% Adsorption	% Desorption	% Adsorption	% Desorption	% Adsorption	% Desorption
1	99.95±0.00	99.79±0.00	99.33±0.00	99.23±0.01	99.25±0.00	94.98±0.01
2	99.88±0.00	99.46±0.00	99.04±0.00	96.99±0.01	99.27±0.00	94.94±0.02
3	99.87±0.00	98.67±0.00	98.35±0.00	95.14±0.02	99.29±0.00	92.80±0.01
4	99.76±0.00	96.26±0.00	96.37±0.00	94.92±0.01	98.28±0.00	93.01±0.01
5	99.08±0.00	95.14±0.00	94.35±0.00	94.24±0.00	98.40±0.00	91.93±0.01
	ANOVA, p-value (<0.001)					

Table 4 outlines results in of adsorpion - desorption efficiencies for the three metal ions.The results indicate that the adsorbents are stable and can be resused with high efficiency of upto the five cycles. The progressive decline in the adsorption-desorption efficiencies with increased number of cycles can be attributed to incremental biomass losses, similar to those reported in sugar-beet peptin gels (Mata *et al.*, 2010) and banana peels (Hossain *et al.*, 2012a).

3.6 Determination of trace metals in real water samples

Copper, lead and cadmium ions were analyzed in river water samples (collected from Chania river in Thika County in Kenya) using the most efficient adsorbent (acid modified watermelon peel). The results obtained are recorded in Table 5.

Table 5: Metal ion concentration and percent (%) recovery of metals in river water

Metal ion	Std. Added (mg/L)	Found (mg/L)	% Recovered
Lead	0.00	0.0476	-
	1.00	0.127±0.001	87.3±0.001
	2.00	0.469±0.012	75.2±0.010
	4.00	1.044±0.004	73.2±0.002
	8.00	2.539±0.001	68.3±0.001
Copper	0.00	0.114	-
	1.00	0.193±0.010	80.7±0.009
	2.00	0.398±0.002	80.1±0.002
	4.00	1.132±0.001	71.7±0.001
	8.00	3.549±0.001	55.6±0.000
Cadmium	0.00	0.062	-
	1.00	0.249±0.01	75.1±0.001
	2.00	0.562±0.004	71.9±0.003
	4.00	1.233±0.002	69.2±0.001
	8.00	3.621±0.001	54.74±0.001

The results confirm the efficiency of MWP in removing the metal ions in river water. The highest recovery was recorded at low concentration with lead recording he highest recovery of 87 % at 1.00 ppm. The results from these tests were in agreement with those obtained with model solution. However the sorption of the metals was found to be relatively lower for the environmental sample. Similar results were reported on use of banana (Renata *et al.,* 2011) and maize tassel (Mwangi *et al*., 2012).

4. Conclusions

In this study, adsorption efficiency of acid modified and unmodified watermelon peels toward removal of Cu^{2+}, Pb^{2+} and Cd^{2+} ions from water was evaluated. The experimental conditions, such as pH, initial metal concentration, dosage of adsorbent and time of exposure greatly influenced the efficiency of removal of the metal ions. Acid modified and unmodified watermelon peels show different levels of efficiency in removing the ions. The adsorption equilibrium data obtained showed best fit with the Langmuir model isotherm. The adsorption kinetic data fitted a pseudo-second-order model well. The changes in MIR spectra of the watermelon peels reflect some changes associated with exposure to the acid. Acid-treated watermelon peels can be regenerated and reused for at least up to five times without reducing their efficiency. A follow-up study is recommended on the adsorption efficiency of watermelon peels for other metals and microbes.

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