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 to 1N 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 Cu²⁺, Pb²⁺ and Cd²⁺ 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 Cu²⁺, Pb²⁺ and Cd²⁺ 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 % Pb²⁺ions, 99.79 % in Cu²⁺ and 99.23 % Cd²⁺ in chemically modified watermelon peels were recorded.

Keywords: Watermelon; 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 °C 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 °C for 24 hours. Each product was then washed with distilled water to remove the excess acid, filtered and kept in sodium bicarbonate solution NaHCO₃ (1 %) overnight to eliminate the acid residue (Khalfi and Menai, 2012; Moyo and Chikazaza, 2013). Finally, each treated adsorbent was dried at 105 °C 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 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.

$$\text{R}^\% = \frac{(C_i - C_e)}{C_i} \times 100$$  \hspace{1cm} (1)

Where, $C_i$ and $C_e$ are the initial and equilibrium metal
concentration The amount of metal adsorbed by natural and
acids treated watermelon was calculated using Equation 2.

$$q_e = \frac{(C_i - C_e)V}{M}$$  \hspace{1cm} (2)

where, $q_e$ is the metal uptake (mg metal adsorbed per g
adsorbent), $C_i$ and $C_e$ 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$_2$SO$_4$ 0.1 mol/L HNO$_3$, 0.1 mol/L
CH$_3$COOH, 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$_2$SO$_4$, 0.1 mol/L HNO$_3$,
0.1mol/L CH$_3$COOH, 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;

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

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;

$$ln q_e = lnK_F + \frac{1}{n}lnC_e,$$  \hspace{1cm} (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 $ln q_e$
versus $ln C_e$ 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:

$$\log(q_e - q_t) = \log q_e - (K_1t/2.303)\hspace{1cm} (5)$$

The pseudo-first-order equation is expressed as:

$$\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{1}{q_e}\hspace{1cm} (6)$$

Where, $q_t$ is the mass of metal adsorbed at equilibrium
(mg/g), $q_e$ 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 $q_e$ 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 $t/q_t$ 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\textsubscript{2}SO\textsubscript{4} treatment are shown in Figure 1.

![SEM images](image1)

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

The SEM images clearly reveal changes in the surface texture and morphology of the watermelon exposed to H\textsubscript{2}SO\textsubscript{4}. Prior to the treatment, watermelon peels have largely plain surface with few large pores (Figure 1a). However, after H\textsubscript{2}SO\textsubscript{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 	extit{et al.}, 2014), in acid modified orange peel (Feng and Guo 2012) and banana peel (Hossain 	extit{et al.}, 2012b).

3.1.2 MIR

![MIR spectra](image2)

**Figure 2:** MIR of unmodified (UMWP) and modified watermelon peels (MWP)

MIR spectra suggest some significant structural changes associated with acid-treatment of watermelon peels. The peaks at 3446 cm\textsuperscript{-1} and 3440 cm\textsuperscript{-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 	extit{et al.}, 2011). The peak observed at 2929 cm\textsuperscript{-1} in both UMWP and MWP is assigned to the symmetric and asymmetric C-H stretching of aliphatic acids. The difference in absorbance intensities associated with C=O at 1737 cm\textsuperscript{-1} and 1735 cm\textsuperscript{-1} in UMWP and MWP reflects other structural modifications that take place during exposure to the acid. The peak at 1627 cm\textsuperscript{-1} in the UMWP is assigned to conjugated C=O stretching and NH\textsubscript{2} deformation in primary amines. The peak at 1633 cm\textsuperscript{-1} appearing in the MWP may also be indicative of N-H bond of primary amine. At 1440 amd 1438 cm\textsuperscript{-1} peaks in UMWP and MWP show the presence of OH stretch in carboxilic acids. At 1390 cm\textsuperscript{-1} and 1176 cm\textsuperscript{-1} new peaks emerge in the modified peels which may be assigned to \textit{SO}\textsubscript{2} symmetrical stretch from sulfonyl chlorides. The peaks at 1272 cm\textsuperscript{-1}, 1278 cm\textsuperscript{-1} and 1106 cm\textsuperscript{-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

![Adsorbent dosage](image3)

(a)
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; Kirthikeyan 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 follow patterns similar to those reported by other researchers with different adsorbents (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 (Muhmmad 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 removal of 98.8% and 120 mins for Cu$^{2+}$ and Cd$^{2+}$ ions with efficiecnes 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 subsequence 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).

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; Kirthikeyan 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 follow patterns similar to those reported by other researchers with different adsorbents (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).

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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).
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$_3$O$^+$) 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

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 Freundlich equation and the results represented in Table 1.

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 134.23 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 capacities for the metal ions were higher in acid modified asorbent as compared to the unmodified 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.

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 modified forms of the adsorbents recorded the higher values of q$^e$, K$\theta$ as compared to the raw forms of the adsorbents. 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 reuse 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 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$_{\text{max}}$ (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 | 0.444 |
| 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 |

| Table 2: Kinetic parameters for asorption of Cu$^{2+}$, Pb$^{2+}$ and Cd$^{2+}$ ions onto MWP and UMWP |
|---|---|---|---|---|---|---|
| Ion | Pseudo- First-Order | | | | | |
| | Adsorbent | q$_e$ (mg/g/min) | k$_1$(mg/g/min) | R$^2$ | 1/n | Kf(mg/g) | R$^2$ |
| Cd | UMWP | 0.114 | 0.009 | 0.199 | 25.000 | 1.52x10$^{-4}$ | 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$^{-2}$ | 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 |

| 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 | 21.42±0.00 |
| Distilled water | 35.92±0.00$^{a}$ | 24.44±0.00 | 42.34±0.00 |
| 0.1M Sulphuric acid | 99.23±0.00$^{a}$ | 75.30±0.00 | 99.79±0.00 |
| 0.1M HCl | 60.55±0.00$^{a}$ | 33.33±0.00 | 45.42±0.00 |
| 0.1M HNO$_3$ | 64.01±0.00$^{a}$ | 25.47±0.00 | 58.89±0.00 |
| 0.1M CH$_3$COOH | 32.87±0.00 | 20.61±0.00 | 38.45±0.00 |
| 0.1M NaOH | 25.81±0.00 | 11.68±0.03 | 22.65±0.00 |
| 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, α=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 reported in the study involving regeneration of banana peels (Hossain et al., 2012b). The recovery and reuse process was continued up to five times using sulphuric acid as shown in Table 4.

![Image](image.png)

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

| Cycles | 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 | 99.98±0.01 |
| 2      | 99.88±0.00 | 99.46±0.00 | 99.04±0.00 | 96.99±0.01 | 99.27±0.00 | 99.44±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 |

Table 4 outlines results in of adsorption - desorption efficiencies for the three metal ions. The results indicate that the adsorbents are stable and can be reused with high efficiency of up to 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 samples (collected from Chania river in Thika County in the adsorbents are stable and can be reused with high efficiencies for the three metal ions. The results indicate that Table 4 outlines results in of adsorption - desorption efficiencies for the three metal ions. The results indicate that the adsorbents are stable and can be reused with high efficiency of up to five cycles.

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 peels). 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±0.00       | 87.3±0.00    |
| 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      | 0.396±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      | 54.7±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 his 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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