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Manganese (VII) Adsorption Kinetics from Aqueous Solutions Using Watermelon (*Citrillus Lanatus*) Peels as Adsorbent

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ABSTRACT

This research work investigated the adsorption of manganese (VII) ions from aqueous solution onto watermelon peels. The study was carried out to assess the possible use of watermelon peels as a low cost adsorbent. The influence of the following factors; contact time and initial metal ion concentration on the adsorption capacity has been studied. The percentage removal of the metal was observed to increase with increase in contact time; 10-40 minutes. The result indicated that activated watermelon peels could be effectively used for the adsorption of Mn(VII) ions from aqueous solutions. First order and second order kinetic studies were carried out. The kinetics study conformed to pseudo second-order model.

KEY WORDS: adsorption, manganese (VII) ions, watermelon peels.

CITATION OF THE ARTICLE



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I. INTRODUCTION

Removal of heavy metals from industrial effluents is a major challenge of waste water treatment. Heavy metals occur as contaminants of liquid waste discharged from various industries such as electroplating, tanneries, textiles, radiator manufacturing, chloralkali, oil refineries, mining and smelting (Kula *et al.*, 2008). The most common toxic metals found in industrial waste water are chromium, nickel, manganese, mercury, cadmium, lead, copper and zinc. Potential exists for the accumulation and exposure of the metals to human and other biological systems via water or food (Farooq *et al.*, 2010). When heavy metals exceed tolerance level, they have a harmful effect on human physiology causing various diseases and disorders among which are neurons and renal breakdown, brain damage convulsions (Kula *et al.*, 2008). 'Heavy metals' refers to any elements with the atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 (Kula *et al.*, 2008).

Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode manganese into waters. Improper disposal of dry-cell batteries or other toxic wastes from industries can yield higher manganese concentrations well above those normally found in environmental water and cause significant harm to public health (Frisbie *et al.*, 2012). Manganese at lower doses is an essential nutrient for humans and animals. Mn at elevated concentrations is a powerful neurotoxin which affects the nervous system and causes learning disabilities and intellectual impairment in children (Bouchard *et al.*, 2011). Studies have shown that children exposed to 240–350 µg manganese/L in water had elevated manganese concentration in their hair and exhibited impaired manual dexterity and speed, short-term memory, and visual identification when compared with children from areas which manganese was controlled (Bouchard *et al.*, 2011). Children exposed to manganese intoxication from water containing above 1,0 µg manganese/L, had attention and memory impairments conditions and others presented neurologic symptoms including a repetitive stuttered speech, poor balance, coordination, and fine motor skills (Lucchini *et al.*, 2009). Manganese intoxication is also linked to Mn induced Parkinsonism, low fetal weight, infant mortality and increased cancer rates (Spangler and Reid, 2010).

Owing to the toxic and adverse effects of heavy metals, most industries are advised to treat waste waters systematically so that the metal contents can be minimized in their wastes. Various conventional treatments have been applied for removing heavy metals such as chemical precipitation, ion exchange, filtration and electrochemical treatment, but most of these methods are only suitable for large scale

treatments and incur high cost to be practiced (Goher *et al.*, 2015). Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge. Numerous approaches have been studied for the development of more effective methods in removing metal pollution and the adsorption process is found to be more practicable over other techniques. Biosorption process is one of the easiest, safest and more cost-effective methods for heavy metal removal from industrial effluents and this process is already established as a simple operation and an easy-handling process (Goher *et al.*, 2015).

When sugarcane bagasse was modified with methanol, however, the resulting adsorbent did not show a good uptake of cadmium as the maximum adsorption capacity was 6.79 mg/g (Ibrahim *et al.*, 2006). The performance of hydrogen peroxide treated bagasse fly ash, a solid waste of sugar industry for removal of lead and chromium was explored by Gupta and Ali (2004). Hydrogen peroxide is a good oxidizing agent and used to remove the adhering organic matter on the adsorbent. It was found that hydrogen peroxide treated bagasse fly ash was able to remove chromium in a shorter period of time (60 min) compared to lead (80 min). Goher *et al.* (2015) investigated the removal of manganese and other metal ions from industrial wastes using granular activated carbon which recorded an adsorption capacity of 2 mg/g for manganese ion removal. This present work illustrates the adsorption of Mn(VII) metal ions from aqueous solutions and the study of the adsorption kinetics; pseudo first-order and pseudo second-order models.

II. MATERIALS AND METHODS

Adsorbent Preparation

Watermelon peels were obtained from local fruit market and washed with tap water followed by doubly-distilled water. After thorough washing, watermelon peels were cut into small pieces and dried under sunlight for seven days. The dried watermelon peels were washed repeatedly with hot water (70 °C) to remove any soluble matter present and then dried in an oven at 85 °C for 48 hours. The oven dried watermelon peels were pounded using mortar and pestle and sieved through a 250 µm sieve. The watermelon peels granules were stored in air tight polyethylene bottles and used for sorption experiment (Augustine and Egila, 2013).

Activation of Adsorbent

A 100 g of the screened adsorbent was soaked in excess of 0.3 M trioxonitrate (V) acid, HNO₃ for 24 hours to remove any debris or soluble biomolecules that might interact with the metal ions during the sorption process. This constitutes the chemical

activation of the sample. The adsorbent was then filtered through whatman No. 41 filter paper and rinsed first with filtrate and then with deionised water. The rinsed adsorbent was later air dried for 12 hours and stored in a plastic can for further experiment (Augustine and Egila, 2013).

pH Determination

The pH value of the prepared adsorbent was determined by soaking 1 g of the sample in 100 mL of deionized water and stirring for 1 hour (Igbokwe and Nwabanne, 2002).

Preparation of Manganese Stock Solution

A stock solution of manganese (VII) were prepared by dissolving 2.887 g of potassium permanganate in 0.1 molar KNO₃. KNO₃ served as an electrolyte to control the ionic strength of the metal ion, the solution was then diluted to 1000 cm³ to give 1000 mg/L. Other concentrations of 60, 80 100 and 120 mg/L from the stock solution were obtained by serial dilution which were used for sorption experiment.

Adsorption Experiment

Biosorption studies were carried out by optimizing the following parameters: contact time and initial metal ion concentration.

Effect of contact time

The effect of contact time on percentage sorption of metal ion, Mn(VII) was investigated over contact time 10, 20, 30 and 40 minutes. A 0.25 g of adsorbent was shaken at 500 rpm with 15 mL of 100 mg/L sorbate concentration. The temperature was maintained at 30 °C. The separation of the adsorbent and solution was carried out by filtration with whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metal ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS).

Effect of Initial Metal Ion Concentration

The effect of initial metal ion concentration on percentage sorption of metal ions, Mn(VII) was investigated for optimizing the initial metal ion concentration, 60, 80, 100 and 120 mg/L. A 0.25 g of adsorbent was shaken at 500 rpm with 15 mL of each of the investigating concentration. The temperature was maintained at 30 °C. the separation of the adsorbent and solution was carried out using whatman filter paper No. 42 and the filtrate stored in sample cans in a refrigerator prior to analysis. The residual metal ion concentrations were determined using an Atomic Absorption Spectrophotometer (AAS).

Calculation of Uptake Capacity for each Sample

The uptake capacity for each sample was calculated as follows;

$$q_e = \frac{(C_o - C_e)v}{m} \dots\dots\dots (1)$$

Where; C_o = initial metal ion concentration $\frac{mg}{L}$

C_e = the equilibrium metal ion concentration $\frac{mg}{L}$

V = volume of the solution in L

m = weight of the adsorbent used in g

Calculation of Percentage Sorption for each Sample

The extent of sorption in percentage was calculated using the equation;

$$\% \text{ sorption} = \frac{C_o - C_e}{C_o} \times 100 \dots\dots\dots (2)$$

Where; C_o= initial metal ion concentration (mg/L)

C_e= final metal ion concentration (mg\ L)

III. GRAPHICAL REPRESENTATION

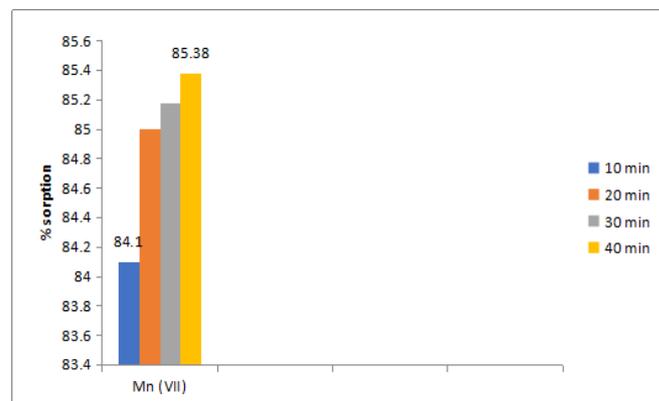


Figure 1: Effect of Contact Time on the Percentage Sorption by Watermelon Peels

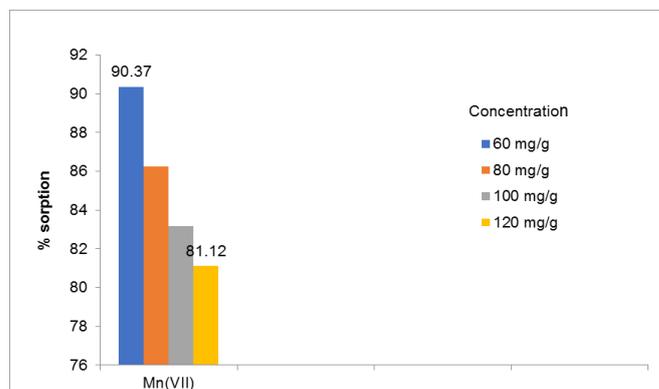


Figure 2: Effect of Initial Metal ion Concentration on Percentage Sorption by Watermelon Peels

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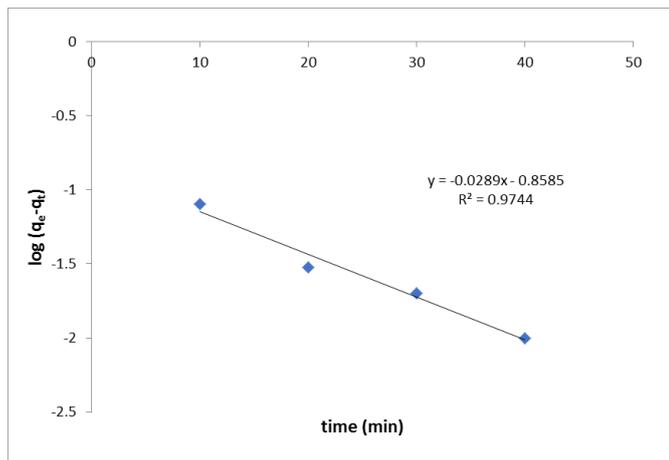


Figure 3: First Order Adsorption Kinetics Plot of Mn(VII)

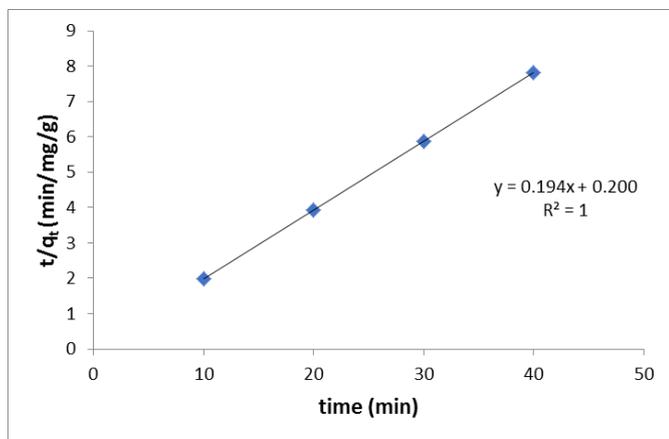


Figure 4: Second Order Adsorption Kinetics Plot of Mn(VII)

IV. RESULTS

Table 1: Kinetic Parameters on the Adsorption of Mn(VII) onto Watermelon Peels

Heavy metal	q _{exp} (mg/g)	Pseudo first order			Pseudo Second order		
		R ²	q _{·cal} (mg/g)	K ₁ (min ⁻¹)	R ²	q _{·cal} (mg/g)	K ₂ (gmg ⁻¹ min ⁻¹)
Mn(VII)	5.130	0.832	0.153	0.064	1.000	5.000	0.206

V. DISCUSSION

Effect of Different Parameters on Adsorption

Effect of Contact Time :

The effect of contact time on the adsorption efficiency is as shown on Fig 1. Adsorption experiments were carried out at different time intervals, 10, 20, 30 and 40 minutes in the metal ion, Mn(VII) . It was observed that adsorption of the tested metal ion was optimum

within a short period of 30 minutes. Adsorption of Mn(VII) increased with increase in contact time. Previous results revealed that removal of heavy metals were rapidly removed within a short period of 30 minutes (Olayinka *et al.*, 2009). The effect of contact time on adsorption process of metal ions from waste waters were studied by many authors (Dakiky *et al.*, 2002).

In addition, manganese with relatively small ionic size 0.39 Å was observed to have been adsorbed at faster rate at equilibrium. This may be explained by considering the ionic radius of manganese being low. This was observed on other biological adsorbents as reported earlier (Horsfall *et al.*, 2004). Thus, the smaller the ionic sizes, the greater the affinity to active sites, and hence the metal ions with smaller ionic radii diffuse faster through the adsorbent pores than the bulkier ones (Egila and Dauda, 2011).

Effect of Initial Metal ion Concentration

The rate of adsorption is a function of initial concentration of metal ions. Figure 2 indicates that higher adsorption was found to take place at lower concentration. This may be due to the interaction of all metal ions present in the solution with binding sites. At higher concentrations, more metal ions are left unadsorbed in solution due to saturation of adsorption sites (Azouaou *et al.*, 2010). The number of ions adsorbed from a solution of higher concentrations is more than that removed from less concentrated solutions.

According to Senthilkumar *et al.* (2000), at lower metal ions concentration, the percentage uptake was higher due to larger surface area of adsorbent being available for adsorption. When the concentration of metal ions became higher, the percentage removal decreased since the available sites for adsorption became less due to saturation of adsorption sites. At a higher concentration of metal ions, the ratio of initial number of moles of metal ions to the adsorption sites available was higher, resulting in lower adsorption percentage.

Adsorption Kinetics

In order to define the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption processes were studied for the contact times ranging from 10 to 40 min and first order and second order models were applied to experimental data as shown in Figures 3-4.

The first order kinetic equation is:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t \dots\dots\dots (3)$$

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Where q_e and q_t are the adsorption capacity at equilibrium and at time t respectively and k_1 is the rate constant of the pseudo first order adsorption process.

Plot of $\log(q_e - q_t)$ versus t gives a straight line for first order adsorption kinetics and the rate constant k_1 is computed from the plot.

The sorption data was also studied by second order kinetics

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \dots\dots\dots (4)$$

The applicability of this equation can be studied by a plot of t/q versus t (Fig 4)

The comparison of experimental sorption capacity (q_{exp}) and the predicted values (q_{cal} , k_1, k_2 , R^2) from pseudo first order, pseudo second order are as given in Table 1. The pseudo first order was not satisfactory to explain the experimental data, whereas the calculated, q_{cal} value derived from the pseudo second order model for sorption of the metal ion was very close to the experimental (q_{exp}) value. The second order equation appeared to be the better fitting model than first order equation because it has higher R^2 value (Azouaou *et al.*, 2010; Gupta and Ali, 2004). This was also in line with a research by Khalid *et al.* (2017) who reported the adsorption kinetics of the biosorption of Cu(II) and Cd(II) ions, indicating that the experimental data were closely aligned with the pseudo second-order equation because the determination coefficient was more than 0.98. The pseudo second-order rate parameter q_e was successful in estimating q_e because the experimental value q_e agreed with the q_e (calculated).

VI. CONCLUSION

Watermelon peels could be used as a very effective low-cost adsorbent for the removal of Mn(VII) ions from aqueous solution considering the maximum percentage removal of the metal ion studied through the various adsorption experiments. Batch studies of manganese removal showed significant effects of the variables: contact time and initial metal ion concentration. The results provide a good indication of the different operating conditions that could be required for efficient removal of the heavy metal from aqueous solutions. Kinetics data was best modeled by a pseudo second order kinetic equation.

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