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RESEARCH ARTICLE

KINETICS, EQUILIBRIUM AND THERMODYNAMICS STUDY ON THE ADSORPTION OF Pb^{2+} IONS BY WATER HYACINTH POWDER FROM BOTH INDUSTRIAL WASTEWATER AND AQUEOUS SOLUTION

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ABSTRACT

In this study, water hyacinth powder was an adsorbent for the removal of Pb^{2+} from an aqueous solution in batch. The individual adsorption capacity of Pb^{2+} by oven dried water hyacinth powder was studied. The study showed that the adsorption of Pb^{2+} is better described by the Langmuir isotherm model and the sorption capacity was found to be 16mg/g. Batch adsorption experiments were conducted were used to examine the effects of particle size, pH, contact time and adsorbent dosage on the removal of Pb^{2+} from aqueous solution by water hyacinth powder. The adsorption efficiency increased with pH and the optimum adsorption was observed at pH 4. Also, the adsorption efficiency of water hyacinth decreased with increase in particle size in the order: $<300, >300<425, >425<2800 \mu m$. The optimum time for adsorption of Pb^{2+} ions was 30 minutes while the optimal adsorption was obtained with 2.5g of the adsorbent. Assessment of kinetics studies showed that the removal of Pb^{2+} followed pseudo-first-order rate equations based on the coefficient of determination R^2 values. The study showed that the use of water hyacinth powder in the removal of Pb^{2+} from aqueous solution is feasible.

KEYWORDS

Water Hyacinth, Batch Studies, Kinetics, Equilibrium, Thermodynamics

1. INTRODUCTION

The occurrence of heavy metals in the surroundings causes alarm because they're poisonous even at low concentrations (Fashola et al., 2016). Heavy metal pollution poses health problems that require being addressed (Hegazi, 2013). Exposure to lead has varied effects which include nausea, brain damage, headache, death, abdominal pain and swelling of optic nerve (Jaishankar et al., 2014). In children it lowers the IQ, causes convulsions while in adults it causes memory loss, damages reproductive organs, nephropathy, insomnia, anorexia, abdominal pain and high blood pressure (Gundogdu et al., 2012). Adsorption method has been widely utilized in the elimination of heavy metals contained in both drinking water and wastewater by utilizing activated carbon. Nonetheless, this method is costly. However, the application of locally available material makes the process relatively inexpensive, energy efficient, environment friendly, easier to design and operate (Cortes-Esquivel et al., 2012; (De Gisi et al., 2016). The objectives of this research were to examine the sorption properties of water hyacinth powder for lead ions. This included the calculation of adsorption capacity and the investigation of pH, particle size, adsorbent dosage and contact time.

2. MATERIAL AND METHODS

2.1 Water Hyacinth Preparation

The water hyacinth stems collected from the Lake Victoria beach were sliced into minute bits and cleaned completely with water in order to eliminate dust and other contaminants. Distilled water was then used to rinse and the stems dried. The water hyacinth pieces were further oven dried at 110 °C for twenty-four hours. The dry fractions of the water hyacinth stem were ground to a fine powder using mortar and pestle and sieved using 300, 425 and 2800 μm sieves. The powder was then stored for subsequent use. All chemicals used in this study were of analytical grades.

2.2 Preparation of the Stock Solutions and Working Solutions

Separate stock solutions of 1000 mg/L of Pb was prepared by dissolving 1.6311g of analytical grade $Pb(NO_3)_2$ in 100 ml double distilled water and diluted to 1L in a 1000ml conical flask. The solutions were then stirred and used for subsequent preparation of working solutions. Working solutions (0.5-80 ppm) was prepared through serial dilution of the stock solution.

2.3 Adsorption Experiments

All the adsorption experiments were conducted in batch process using 0.5g of water hyacinth powder of $<300 \mu m$ with 100ml of lead solution. Initially, the adsorption studies were carried out in 500ml Erlenmeyer flasks varying one parameter at a time. The flasks containing both water hyacinth powder and the adsorbate were stirred at 300 rpm at room temperature. The samples were taken at predetermined time intervals of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110 and 120 minutes. The time interval that gave the optimum adsorption efficiency was used for the subsequent experiments. The effects of particle size was studied using $<300, >300<425, >425<2800 \mu m$ while those of pH were evaluated in the range of pH 2-7. With optimum pH, contact time and particle size, the effects of adsorbent dosage was assessed with adsorbent dose used ranging from 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5 and 5.0g. Each study was conducted thrice and the mean value obtained. After the adsorption, the mixture was filtered using Whatman filter paper no 40 and the residual concentration determined using Atomic Absorption Spectrophotometer (AA-6300 Shimadzu). The adsorption efficiency (a) and the adsorption capacity (q) of water hyacinth were calculated based on C_1 and C_2 using the equations 1 and 2 respectively.

$$a = \frac{C_1 - C_2}{C_1} \times 100 \quad (1)$$

$$q = \frac{(C_1 - C_2)}{M} \times V \quad (2)$$

Where: a- adsorption efficiency, q- adsorption capacity, C₁ and C₂- initial concentration and final concentrations respectively, M-mass of the adsorbent, V-volume of the aqueous solution.

The data obtained from the experiment was fitted in linear form of Langmuir and Freundlich isotherms to characterize the reaction mechanism. The equilibrium adsorption capacity, q_e (mg/g) for water hyacinth was calculated using Equation 3

$$q_e = \frac{(C_0 - C_e)v}{w} \tag{3}$$

Where: C₀ and C_e are the initial concentration and final equilibrium concentration of the heavy metal (mg/L), v (L) and w (g) are volume of the sample and mass of the adsorbent used respectively.

The linear form of Langmuir isotherm that was used in studies is shown in equation 4.

$$\frac{1}{q_e} = \left(\frac{1}{q_m b}\right) \cdot \frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

Where: q_e (mg/g) – equilibrium adsorption capacity, C_e (mg/l)- the amount of adsorbed heavy metal ion at equilibrium, q_m (mg/g)- the highest amount of the heavy metal ion for every unit weight of water hyacinth while b (l/mg)- Langmuir constant $\frac{1}{q_e}$ was plotted against against $\frac{1}{C_e}$. The q_m and b values were determined graphically. The linear form of Freundlich isotherm that was used in studies is shown in equation 5

$$\log q_e = \frac{1}{n} \log C_e + \log K_f \tag{5}$$

Where q_e (mg/g) – equilibrium adsorption capacity, C_e (mg/l)- the amount of adsorbed heavy metal ion at equilibrium, K_f- a constant indicating adsorption capacity, n- Adsorption intensity

Log q_e was plotted against log C_e and the gradient of $\frac{1}{n}$ and intercept of log K_f was used in comparing the correlation coefficient, r.

3. RESULTS AND DISCUSSIONS

3.1 Effects of Particle Size

The quantity of Pb²⁺ adsorbed from aqueous solution increased with decrease in particle size in the order >425<2800, >300<425 and <300 μm for the lead concentrations of 75.3 ppm (Figure 1). It was observed that the smaller particles had the highest adsorption efficiency. This is so since they have a larger surface area for adsorption than the larger particles (Akafu et al., 2019). This means area the lower the surface area the lower adsorption efficiency area, the higher the surface area the higher the adsorption efficiency (Schalow et al., 2007). Results similar to this were obtained where lead ions were adsorbed by pumpkin pods (Eze et al., 2013).

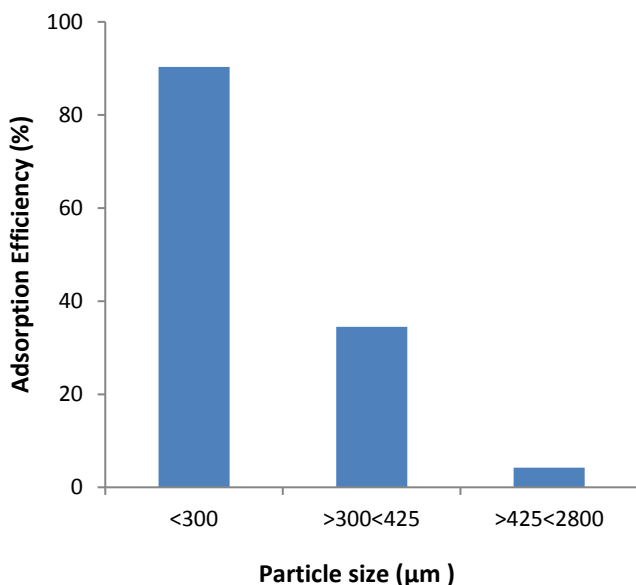


Figure 1: Effects of particle size on adsorption of Pb²⁺ ions from aqueous solution (Adsorbent dose: 0.5g; pH=6.7; contact time 120 minutes; temperature 25±20C)

3.2 Effect of pH

The effects of pH on adsorption of Pb²⁺ on water hyacinth powder are shown in Figure 2. The adsorption efficiency increased as pH increased from 2-4. This might be because of availability of unoccupied adsorption sites. However, there is slow increase in the amount of lead ions adsorbed at the pH above 4. This could be attributed to the fact that the adsorption sites were saturated with metal ions. Results similar to this were obtained by where lead ions were adsorbed by activated carbon prepared from marine green Algae (Jeyakumar and Chandrasekaran, 2014). Beyond the pH 6, the adsorption efficiency started declining. This could be due to precipitation of Pb(OH)₂.

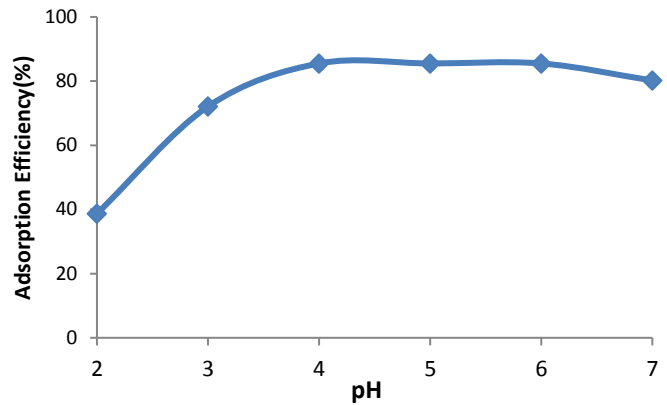


Figure 2: The effects of pH on adsorption of Pb²⁺ ions on water hyacinth from aqueous solution. (Adsorbent dose: 0.5 g; particle size <300 μm; contact time 120 minutes; temperature 25±2 0C)

3.3 Effect of Contact Time

The study showed that the percent lead ion adsorbed by water hyacinth increased with contact time as shown Figure 3. The rapid increase in the first 30 minutes could be attributed to the availability of unoccupied adsorption sites. Adsorption efficiency reached a steady state at 30 minutes. The slow increase after 30 minutes could be resulted from the repulsive force between lead ions bound on the adsorption site and the lead ions present in the solution became stronger hence slow establishment of equilibrium (Mondal et al., 2015).

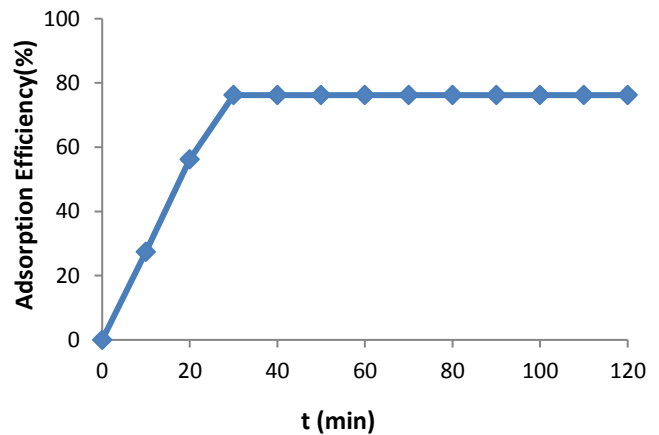


Figure 3: Effects of contact time on adsorption of lead ions from aqueous solution. (Adsorbent dose: 0.5 g; pH = 6.7; particle size <300 μm; temperature 25±2 0C)

3.4 Effect of Adsorbent Dosage

The effects of adsorbent dosage on adsorption of lead ions from an aqueous solution are shown in Figure 4. The percent lead ions adsorbed increased as the amount of adsorbent increased. The increase could be because of increased availability of vacant adsorption sites that increased with the quantity of adsorbent (Annan et al., 2021; Jeyakumar and Chandrasekaran, 2014). The percent lead ions adsorbed then became steady with increase in adsorbent. This could have been because of the shielding effects among the cells (Gao et al., 2009; Gundogdu et al., 2012). This might have produced a block of cell active sites which increased as the adsorbent dose increased (Desta, 2013). The optimum adsorption was 2.5g.

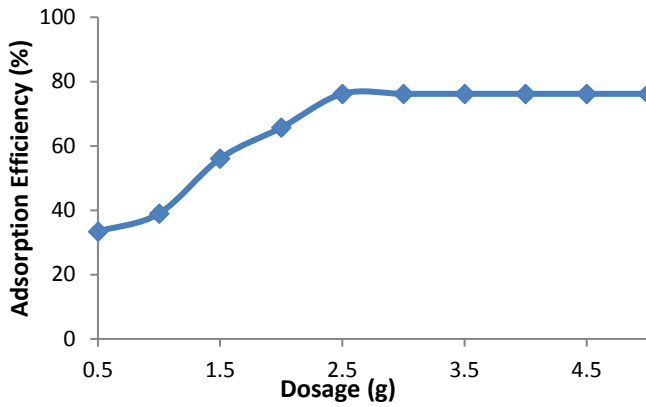


Figure 4: The effects of adsorbent dosage on adsorption of lead ions (Adsorbent dose: 0.5 g; pH = 6.7; particle size <300 μm; contact time 120 minutes; temperature 25±2 OC)

3.5 Adsorption Isotherms

In this study the amount of lead ions adsorbed by water hyacinth powder was investigated using the Freundlich and Langmuir isotherms as shown in Figures 5 and 6 respectively. The study revealed that the logarithm of q_e (adsorption capacity at equilibrium) increased linearly to the logarithm of C_e (concentration at equilibrium). It was observed that the reciprocal of q_e (adsorption capacity at equilibrium) increased linearly with the reciprocal of C_e (concentration at equilibrium). The Freundlich adsorption parameters (equilibrium constant (K_f), n and regression constant (R^2)) and the Langmuir parameters (q_m -the highest quantity of the heavy metal ion for every entity weight of water hyacinth, b -Langmuir constant and regression constant (R^2)) were determined graphically from Figure 5 and 6 the results are presented in Table 1. The use of water hyacinth powder on the adsorption of lead ions correlated well with the Langmuir model in contrast to the Freundlich model based on the R^2 values. Results similar to this were obtained where lead ions were adsorbed by coal based activated carbon (Yi et al., 2016).

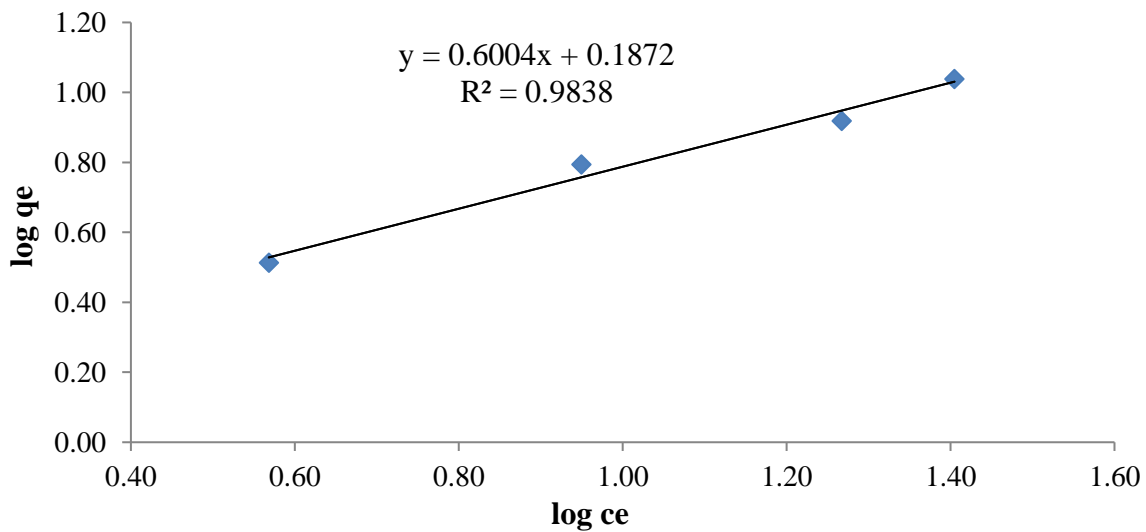


Figure 5: Linearized Freundlich plot for the adsorption of lead ions onto water hyacinth powder

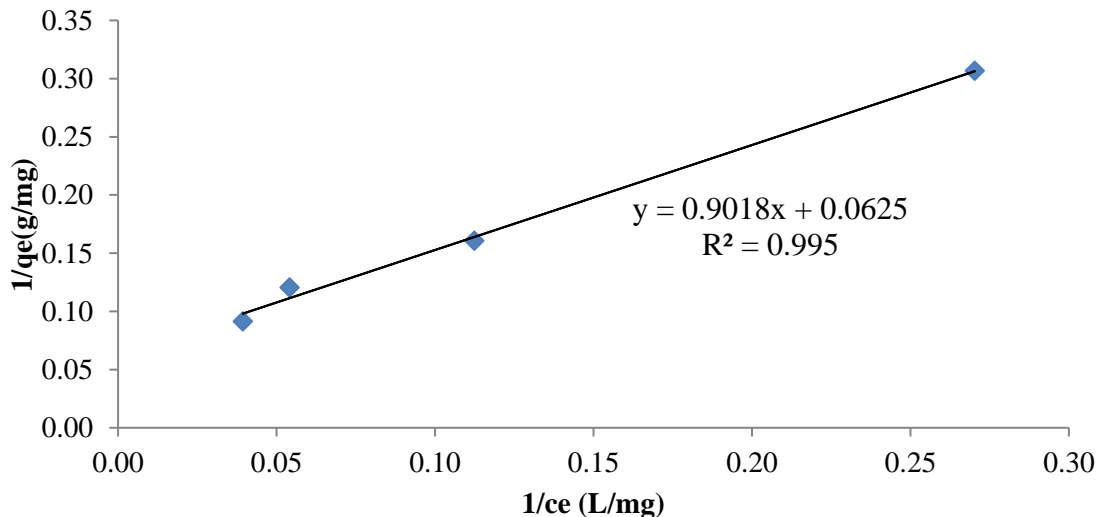


Figure 6: Linearized Langmuir plot for the adsorption of lead ions onto water hyacinth powder

Table 1: Langmuir and Freundlich Isotherms Parameters for Adsorption of Lead Ions from Aqueous Solution Ground Using Water Hyacinth Powder	
Freundlich Isotherm	Langmuir Isotherm
$n = 1.6656$	b (L/mg) = 0.0693
$K_f = 1.5389$	q_m (mg/g) = 16
$R^2 = 0.983$	$R^2 = 0.995$

3.6 Adsorption Kinetic Models

The data obtained in the study was tested against the pseudo-first and pseudo second- order models and results are shown in Figures 7 and 8 respectively. The logarithmic difference in adsorption capacity at equilibrium and at particular time ($\log q_e - q_t$) decreased linearly as the adsorption time increased. The quotient of t/q_t increased linearly with the adsorption time (Boulaiche et al., 2019). The kinetic data for Pseudo-first order and Pseudo-second order parameters for the adsorption from 75.3 ppm lead ionic solution were calculated graphically and the results

are given in Table 2. It was observed that the R² value for Pseudo-first order in the adsorption of lead (R²= 0.929) was higher than that of pseudo-

second order. This suggested that the adsorption kinetics of lead on water hyacinth powder is better expressed by the pseudo first order model.

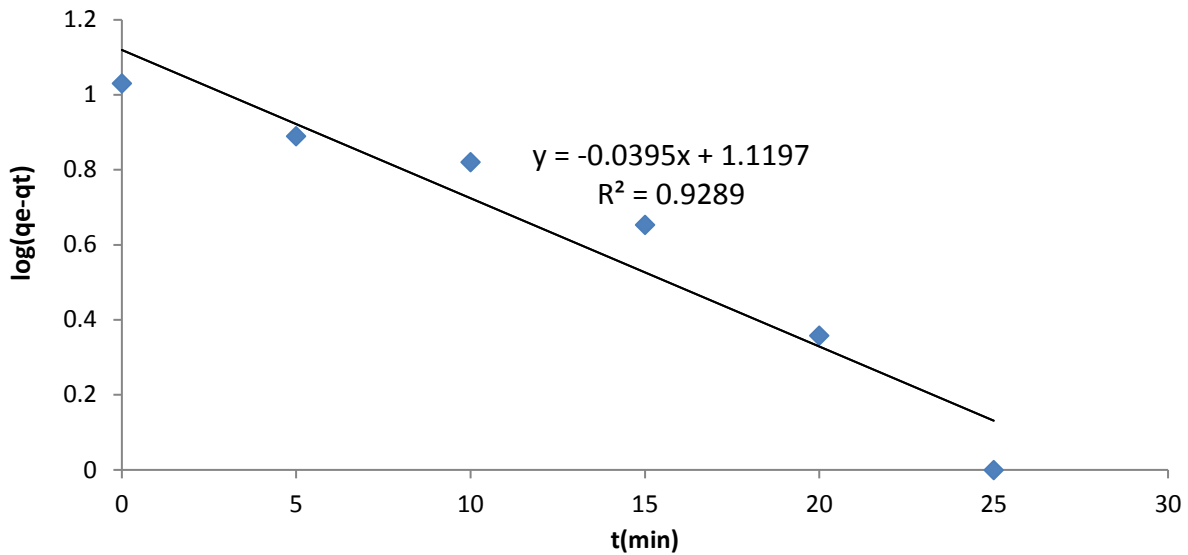


Figure 7: Pseudo-first order for the adsorption of 75.3 ppm Pb²⁺ ions onto water hyacinth powder

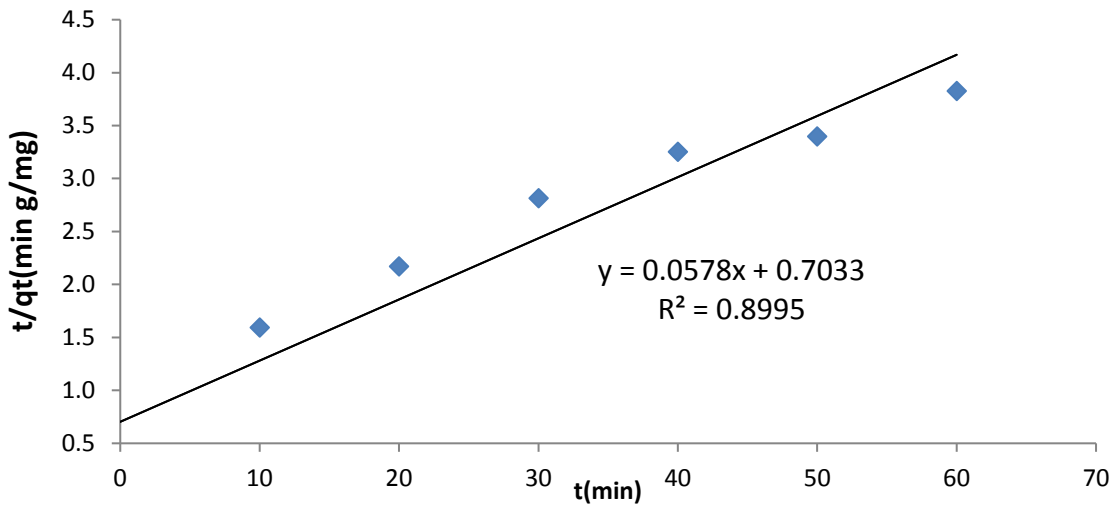


Figure 8: Pseudo-second order for the adsorption of 75.3 ppm Pb²⁺ ions onto water hyacinth powder

Table 2: The Pseudo First-Order and Pseudo Second-Order Kinetic Parameters of Adsorption of Lead Ions on Powdered Water Hyacinth.						
	Pseudo –first order			Pseudo –second order		
	Parameters			Parameters		
Metal ions	K ₁ (min ⁻¹)	q _e (mg/g)	R ²	K ₂ (g/mg/min/)	q _e (mg/g)	R ²
Lead ions	0.0910	13.1735	0.929	0.0069	12.80	0.583

4. CONCLUSION

Adsorption of Pb²⁺ on water hyacinth (*E. crassipes*) powder was influenced by factors such as; adsorption time, dosage, pH and particle size of the adsorbent. The adsorption efficiency increased with increase in contact time. The optimum adsorption time was 30 minutes respectively. The adsorption efficiency increased with the increase in adsorption dosage. Optimum adsorption was observed with adsorbent dosage of 2.5 g. The adsorption of lead ions increased with decrease in particle size in the order >425<2800, >300<425 and <300 μm. The adsorption data for lead from the aqueous solution fitted well in Langmuir. The adsorption data followed the pseudo first order reaction kinetic model. The results obtained from this study indicated that water hyacinth powder could be used for the removal of the industrial wastewater containing lead ions.

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