
Use of unmodified orange peel for the adsorption of Cd(II), Pb(II) and Hg(II) ions in aqueous solutions

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Abstract: Ground orange peel (GOP) was used as adsorbent for Cd(II), Pb(II) and Hg(II) ions in aqueous solutions. Several experiments with variation of some factors namely: initial concentration of the heavy metal ions, contact time, temperature and pH were carried out. FT-IR spectrum of GOP showed the presence of different functional groups on its surface. Equilibrium data were analysed by Langmuir, Freundlich, and Temkin isotherms. Hg (II) and Cd (II) adsorptions were better described by Temkin isotherm while that of Pb (II) was best described Freundlich isotherm. Pseudo second order kinetics with higher R^2 values described adsorption in all cases. Adsorption of Hg (II) was maximum at pH 4, while those of Cd (II) and Pb (II) ions were maximum at pH 6. Thermodynamics study showed that the adsorption processes of Pb(II) and Hg(II) ions were endothermic while that of Cd(II) ions was exothermic in nature.

Keywords: Orange Peels Adsorbent, Adsorption Isotherms, Kinetics, Thermodynamics, pH

1. Introduction

Waste water or aqueous solutions from the food, colouring, paper, paints, carpets, rubber, plastics, cosmetics, textile and other commercial based industries are polluted by heavy metals [1-3]. The presence of very low concentrations of these metals in these effluents (less than 1mg/l for Pb, Cd and Hg) is highly visible and undesirable [3,4]. Heavy metals do not degrade into harmless end products in their metabolism and they are accumulated in the food chain: water--plants--animals--humans; thereby posing the greatest threat to the living organism[5]. Effluents from industries can pollute our plants and thus affect humans greatly. Some brewing industries make use of tanks coated with lead which also can contaminate the drinks which we take. More so some of these industries release heavy metals as gases through their chimneys which when inhaled can be dangerous to our system especially the lungs. Therefore it is advisable to site these industries in non-residential areas [6]. Long term exposure to heavy metals can lead to renal dysfunction, obstructive lung disease in humans and has been linked to lung cancer and bone defects [7]. Emissions of lead into the air have caused considerable pollution. Children are particularly susceptible to lead exposure due to high

gastrointestinal uptake and the permeable blood-brain barrier [8]. Cadmium emissions have also increased dramatically during the 20th century because cadmium-containing products are rarely re-cycled, but often dumped together with household waste. Chronic exposure to elevated level of cadmium is known to cause renal dysfunction (Fanconi syndrome), bone degradation (itai-itai syndrome), cancer, hypertension, liver damage, and blood damage [9]. The usage of mercury is widespread in industrial processes and in various products (e.g. batteries, lamps and thermometers). It is also used as amalgam for dental fillings and by the pharmaceutical industry. The presence of mercury in fish, waste water, dental amalgams, vaccine preservatives, and in the atmosphere has made this particular toxic metal an increasing focus for health authorities and interest groups [10, 11].

There are numerous methods for the removal of metal ions from aqueous solutions and these include: adsorption, membrane separation processes ion-exchange, floatation, electro dialysis, precipitation, reverse osmosis, coagulation etc.[12]. Adsorption is an important and effective technique but the use of some adsorbents like activated carbon has been seen to be expensive for developing countries[13]. This has encouraged research into discovering materials that are both efficient and cheap for scavenging heavy metal ions in

industrial waste water[1]

In this work, orange peels were sourced and used as low-cost adsorbent to remove Hg(II), Cd(II) and Pb(II) ions from aqueous solutions. FT-IR analysis, kinetics, equilibrium, thermodynamics, pH studies were employed to evaluate adsorption parameters.

2. Materials and Methods

2.1. Preparation of Adsorbent Materials and Characterization

The orange peels used were collected from Oja market, Mafoluku, Oshodi, Lagos State, Nigeria. They were sun-dried to remove the moisture and to ease grinding and then ground to fine particles with a laboratory blender, sieved to obtain desired particle size of 300nm and stored in a desiccator for later use.

Functional groups present on the orange peels surface were determined by the FT-IR spectroscopy. The KBr pastille method was used for the orange peels sample preparation. About 2mg of dried orange peels and 200mg KBr were mixed and pulverized to obtain a transparent pellet. The reference measurement was performed with pure KBr and the FT-IR spectra were recorded on an M.530 FT-IR detector in the range of 4000-400 cm^{-1} with a resolution of 2 cm^{-1} .

2.2. Reagents and Metal Solutions

All the primary chemicals used in this study were of analytical grade and used without further purification. The stock solution of 1000mg/l of Cd(II), Pb(II) and Hg(II) ions were prepared by dissolving: 2.743g of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, 1.60g of $\text{Pb}(\text{NO}_3)_2$ and 1.71g of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ respectively in 100ml of deionized water and then made up to in 1000ml in conical flasks. All required concentrations were prepared by serial dilution of the stock solutions. Solutions of 0.5M NaOH and 0.5M H_2SO_4 were used for pH adjustment.

2.3. Adsorption Studies Experiments

For the adsorption studies, five beakers were filled with 100ml of each metal ion solution of varying concentrations (10-50mg/l). 5g of ground orange peels(GOP) was added to each beaker. The mixture was thoroughly stirred with a stirrer and allowed to stand for 45mins after which 10ml was drawn out and filtered. The filtrate was analyzed using the Atomic Absorption Spectrophotometer AAS (240 FS AA.). In all cases the amount of ions q adsorbed per unit weight of adsorbent at time t and removal efficiency (R) were calculated as:

$$q = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Where q is the amount of heavy metal ions adsorbed in mg/l, C_0 is the initial concentration of the metal ion in mg/l, V is the volume of the solution in litres, and C_e is the equilibrium metal ion concentration in mg/l and W is the mass of adsorbent in grams

The kinetics of adsorption was studied at various times of 5, 10,30,60,90 and 120mins. 5g each of GOP was added into six beakers, each containing 100ml of 40mg/l of the metal ions. Concentration and pH constant were kept constant at room temperature. The mixtures were mechanically stirred and left to stand. 10ml of the mixture was drawn out at the end of each interval and filtered. The filtrate was analysed using the Atomic Absorption Spectrophotometer.

Thermodynamics experiments were carried out at temperatures of 50°C, 70°C and 90°C. 5g of GOP each was added into three different beakers containing 40mg/l of the metal ions solution. The mixtures were vigorously shaken, placed in a thermostat water bath already set at 50°C. These were allowed to stand for one hour after which 10ml of the mixture was drawn from each of the beakers separately, filtered and analysed. The above procedure was repeated at temperatures of 70°C and 90°C.

The effect of pH on adsorption of the metal ions was studied over the pH range of 2-8. 100 ml of 40mg/l of $\text{Pb}(\text{NO}_3)_2$ solution was measured into different beakers. The pH was adjusted from 2-8 using 0.5M H_2SO_4 and 0.5M NaOH. 5g of bean husk was added into each beaker and stirred. The mixture was allowed to stand for one hour after which 10ml was drawn out and filtered for analysis. This procedure was repeated using $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ solutions.

3. Results and Discussions

3.1. FT-IR Analysis

In order to identify some main characteristics functional groups in GOP (fresh and metal-adsorbed), infra-red analyses were carried out and the spectra are shown in fig.1 (a-d). The FT-IR spectrum of GOP indicated hydroxyl, amino and carbonyl groups were present on its surface. The broad vibration around 3080 cm^{-1} -3500 cm^{-1} is indicative of the presence of hydroxyl (-OH) and amino(-NH₂) groups of carboxylic acids and amides on the surface of GOP. After adsorption of Cd(II), Pb(II) and Hg(II) ions it was observed that there is slight shift in both absorption wavelengths: Cd(II):3022 cm^{-1} -3775 cm^{-1} , Pb(II):3213 cm^{-1} -3599 cm^{-1} and Hg(II):3132 cm^{-1} -3759 cm^{-1} . The peaks at 1582 cm^{-1} -11767 cm^{-1} were attributed to stretching vibration of carbonyl group (-C=O). It was clearly observed that this bands were shifted to higher wavelengths after metal adsorption: Cd(II)= 1637 cm^{-1} -1834 cm^{-1} , Pb(II)=1664 cm^{-1} -1882 cm^{-1} and Hg(II)=1591 cm^{-1} -1826 cm^{-1} . This confirmed that deprotonated carbonyl groups were involved in adsorption of Cd(II), Pb(II) and Hg(II) onto GOP. The band 1082 cm^{-1} can be assigned to the stretching vibration of C-O. This band was clearly shifted after metal adsorption to higher wavelengths of 1088 cm^{-1} for Pb(II) and lower wavelengths of 1001 cm^{-1} for Hg(II) and 1005 cm^{-1} for Cd(II).

The shifts in the adsorption peaks generally observed indicates the existence of a metal binding process taking place on the surface of the orange peels.

3.2. Adsorption Kinetics

A kinetic study of adsorption is necessary as it provides the information about the adsorption mechanism which is crucial for the practicality of the process. In this work, two kinetic models were applied in order to establish which of them shows the best fit with experimentally obtained data.

The pseudo first order is frequently used to predict metal adsorption kinetics [14]. The rate law for a pseudo-first-order reaction is given as:

$$\ln (q_{e(\text{expt})}-q_t) = \ln C_{e(\text{theo})} - k_1 t \tag{2}$$

Where $k_1(\text{min.g/mg})$ is the rate constant of pseudo first order adsorption, q_t is the amount of metal in (mg/g) adsorbed at any time, $q_{e(\text{expt})}$ is the amount of metal in (mg/g) adsorbed at equilibrium time obtained from experiments, $q_{e(\text{theo})}$ is the amount of metal in (mg/g) adsorbed at equilibrium time obtained from theoretical model. Thus the rate constant k_1 and $q_{e(\text{theo})}$ can be obtained from the slope and the intercept of the plot of $\ln (q_e-q_t)$ against t (fig 2) respectively.

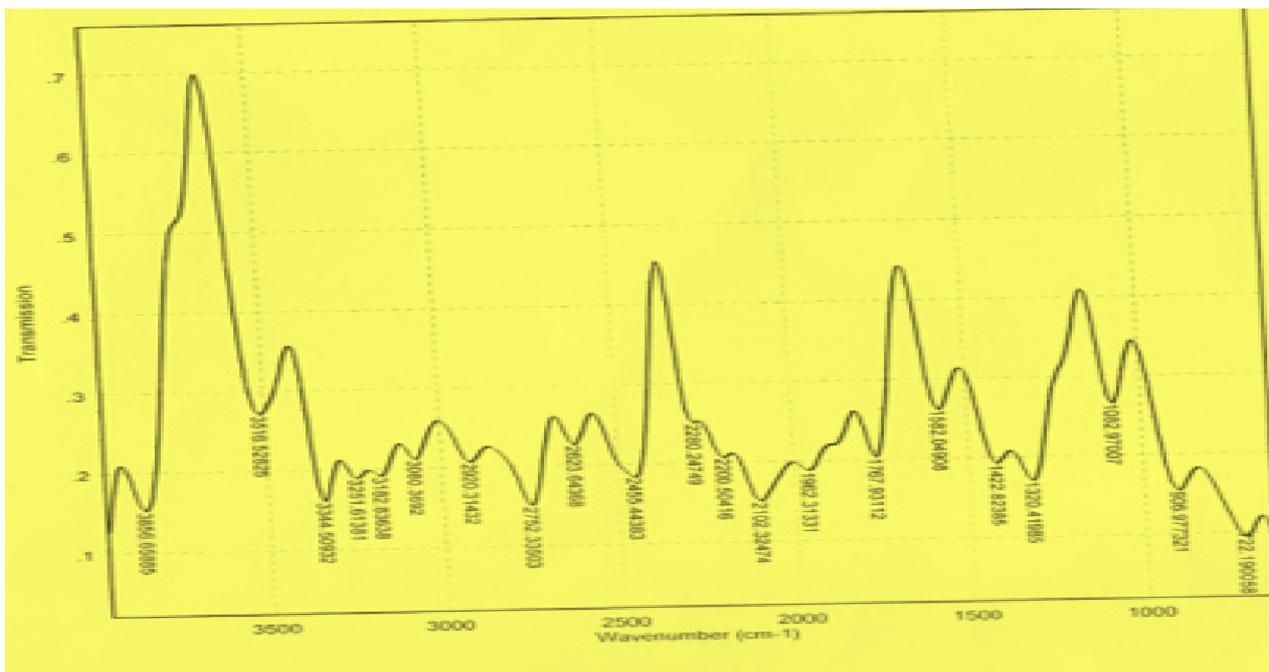


Fig. 1(a). FT-IR spectrum of GOP

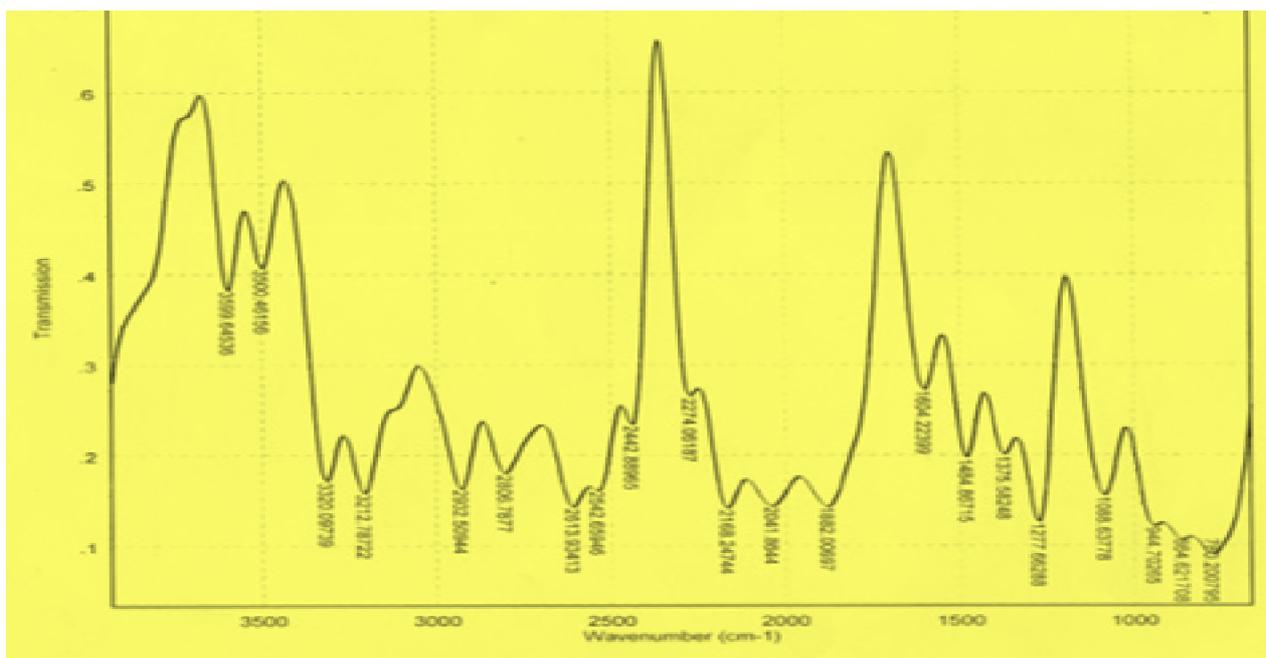


Fig. 1(b). FT-IR spectrum of GOP- Pb (II) ion

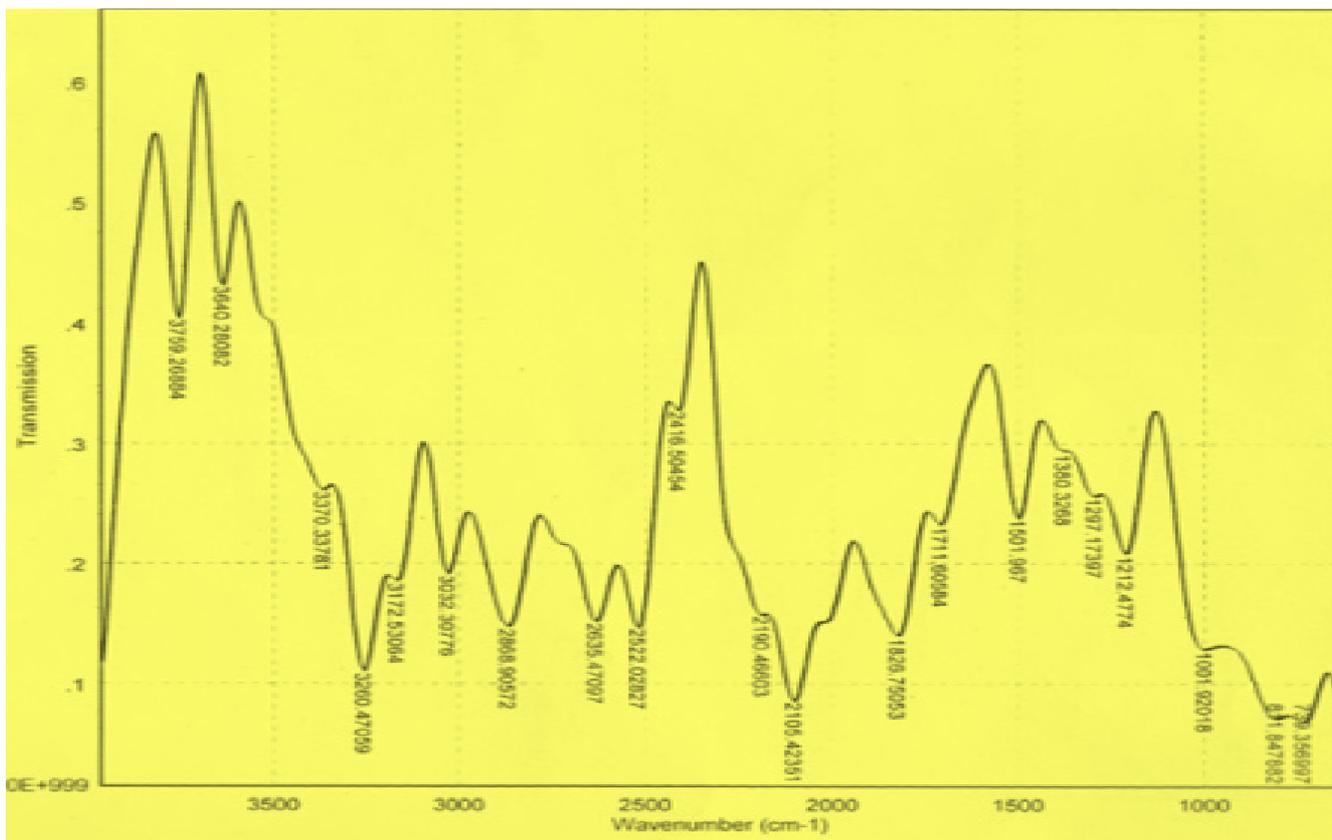


Fig. 1(c). FT-IR spectrum of GOP- Hg(II) ions

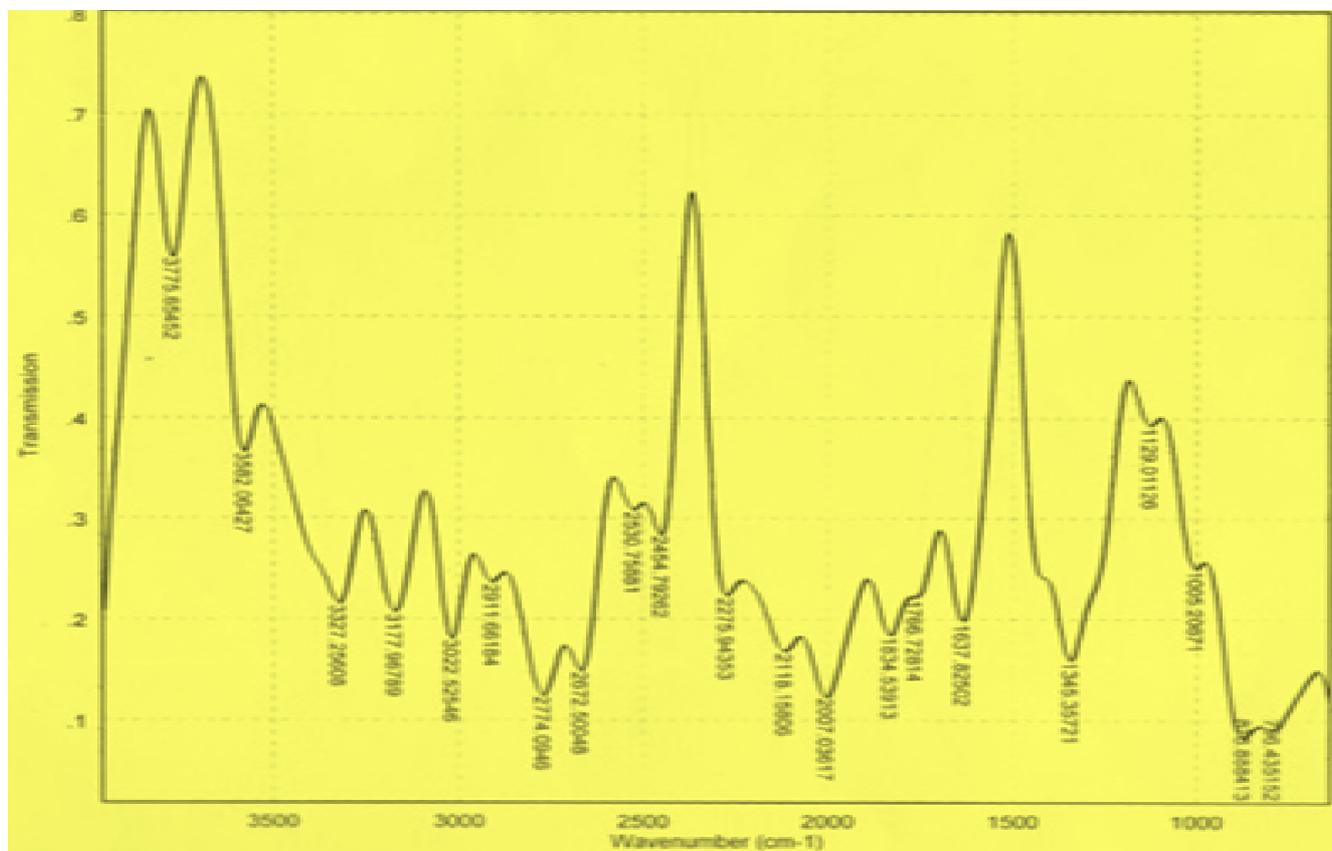


Fig. 1(d). FT-IR spectra of GOP- Cd (II) ions.

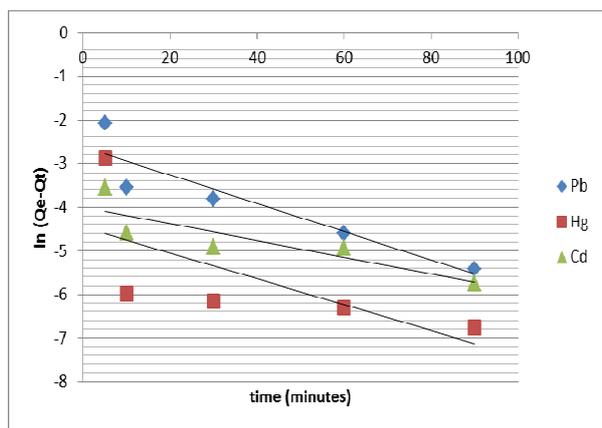


Fig. 2. Pseudo first order plot of adsorption.

The pseudo second order kinetic model may be expressed by the equation[14]:

$$\frac{t}{q} = \frac{1}{K_2 q_e(\text{theo})^2} + \frac{1}{q_e(\text{theo})} t \quad (3)$$

Where k_2 (g/mg min) is the equilibrium rate constant for the pseudo second order adsorption and can be obtained from the plot of t/q against t .

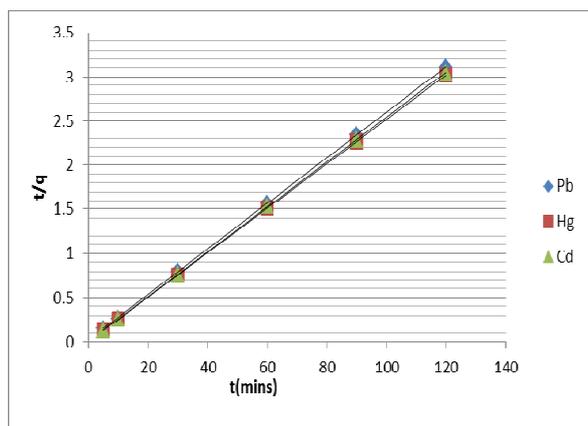


Fig. 3. Pseudo second order plot for the adsorption.

Kinetic parameters for the adsorption of the metal ions onto GOP are tabulated (Table 1). The measure of the fit of two models is verified by the correlation coefficient of determination R^2 . Comparing the R^2 values for the two models shows that the pseudo second order kinetics model gave a better fit in all cases with R^2 values of 1. This implies that 100% of all the observed experimental data was replicated by the second order kinetics. Pseudo second order kinetics model implies that the predominant process here is chemisorption which involving covalent bonding between the adsorbate and the surface of the adsorbent. Chemisorption is usually restricted to just one layer of molecules on the surface, although it may be followed by additional layers of physically adsorbed molecules [15]. Values of $q_e(\text{theo})$ obtained from the second order kinetics model were also much higher than those obtained from the first order kinetics;

further indicating that adsorption processes were better described by the former.

Table 1. Kinetics parameters for the Adsorption of Pb(II), Cd(II) and Hg(II) ions

| Metal ions | First order | | | | Second order | | |
|------------|---------------------------|---------------------------|--------------|--------|---------------------------|-------------------------|-------|
| | $q_e(\text{expt})$ (mg/g) | $q_e(\text{theo})$ (mg/g) | k_1 (/min) | R^2 | $q_e(\text{theo})$ (mg/g) | $k_2 \text{ min.}$ g/mg | R^2 |
| Hg(II) | 0.7960 | 0.0115 | 0.0244 | 0.4521 | 39.84 | 0.124 | 1 |
| Pb(II) | 0.7727 | 0.0722 | 0.0323 | 0.8519 | 38.91 | 0.0291 | 1 |
| Cd(II) | 0.7888 | 0.0186 | 0.0193 | 0.755 | 39.53 | 0.09277 | 1 |

3.3. Adsorption Isotherms

The adsorption isotherm indicates how molecules of adsorbates are partitioned between the adsorbents and the liquid phase at equilibrium. In this study, the equilibrium data obtained for the adsorption of Pb(II), Cd(II) and Hg(II) ions onto GOP were analysed using the Langmuir, Freundlich and Temkin isotherms models[16-18]

The linear form of Langmuir isotherm equation is given as

$$q_e = \frac{q_m K_1 c_e}{1 + K_1 c_e} \quad (4)$$

The reciprocal of the equation above yields

$$\frac{1}{q_e} = \frac{1 + K_1 c_e}{q_m K_1 c_e} = \frac{1}{q_m K_1 c_e} + \frac{1}{q_m} \quad (5)$$

A plot of $1/q_e$ against $1/C_e$ gives a straight line graphs(4-6) with $1/q_m$ as the intercept and $1/q_m k_1$ as slope. Langmuir isotherm is frequently evaluated by a separation factor, R_L , which is expressed as follows

$$R_L = \frac{1}{1 + K_L C_o} \quad (6)$$

Where C_o is the initial solute concentration. The value of separation indicates the shape of the isotherm and the type of the adsorption. Considering the R_L value, adsorption can be irreversible ($R_L=0$), favourable ($0 < R_L < 1$) hence ($R_L=1$) or unfavourable ($R_L > 1$)[19].

Freundlich isotherm is purely empirical and it best describes the adsorption on heterogeneous surface[20]. The Freundlich isotherm equation is shown below in its linear form:

$$\ln q = \ln k_F + \frac{1}{n} \ln C_e \quad (7)$$

k_F in mg/l and n are Freundlich constants related to sorption capacity of the adsorbent and energy of adsorption respectively. These constants are evaluated from the plot of $\ln q$ versus $\ln C_e$ figs(7-9).

Temkin isotherm is represented by the Linear equation as follows;

$$q_e = \frac{R_T}{b_T \ln C_e} + \frac{R_T}{b_T \ln K_T} \quad (8)$$

K_T and b are Temkin constants, R is universal gas constant (8.314J/K/mol) and T is temperature in Kelvin. A plot of q_e

vs. $\ln C_e$ (figs 10-12) gives a slope and an intercept from which b and k_T are evaluated[21-22].

The isotherm parameters for the adsorption of Cd (II), Pb(II) and Hg(II) ions onto GOP are given in Table 2. Temkin model described the adsorption of both Hg(II) and Cd(II) best with R^2 values of 0.9248 and 0.9128 respectively. The adsorption of Pb(II) was best described by the Freundlich model with R^2 value of 0.8822. The R_L values were found to be less than one ($R_L < 1$) for Pb(II), Cd(II) and Hg(II) on their adsorptions to orange peels shows a favourable adsorption. Maximum adsorption capacity follows the trend Cd(II) > Hg(II) > Pb(II). n values for adsorption were all less than 1, indicating. K_F sorption capacity values according to Freundlich were more than the sorption capacity q_m obtained from both Langmuir.

Table 2. Isotherm parameters for adsorption of Pb(II), Cd(II) and Hg(II) ions.

| Model | Parameters | Hg(II) | Pb(II) | Cd(II) |
|------------|--------------|--------|--------|--------|
| Langmuir | q_m (mg/g) | 7.4619 | 5.7644 | 9.0365 |
| | K_L (l/mg) | 1 | 1 | 10.02 |
| | R^2 | 0.6959 | 0.835 | 0.643 |
| | R_L | 0.342 | 0.561 | 0.267 |
| Freundlich | K_F (mg/g) | 10.143 | 7.285 | 12.013 |
| | N | 0.5596 | 0.7675 | 0.3592 |
| Temkin | R^2 | 0.8437 | 0.8822 | 0.7192 |
| | R^2 | 0.9248 | 0.063 | 0.9128 |

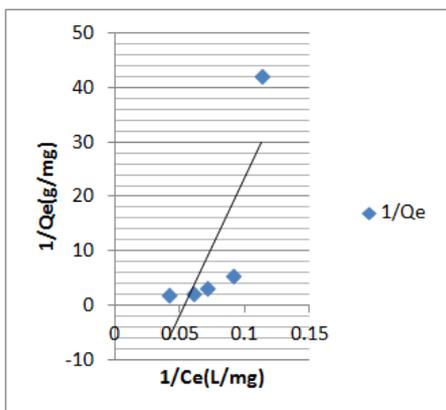


Fig. 4. Langmuir isotherm plot for Cd(II)

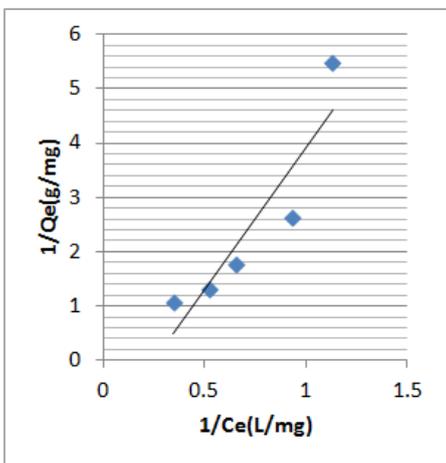


Fig. 5. Langmuir isotherm plot for Pb(II)

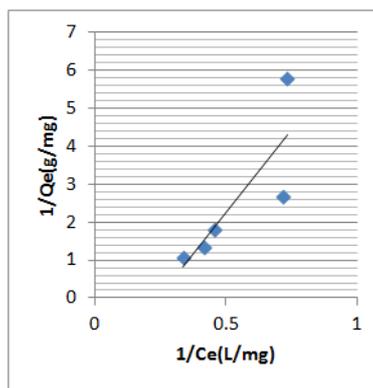


Fig. 6. Langmuir isotherm plot for Hg(II)

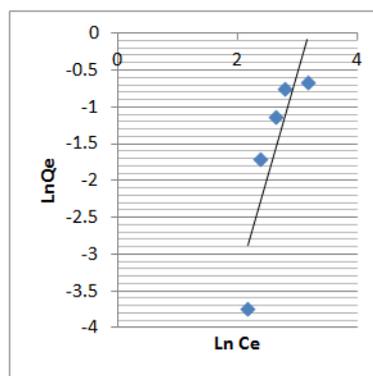


Fig. 7. Freundlich isotherm plot for Cd(II)

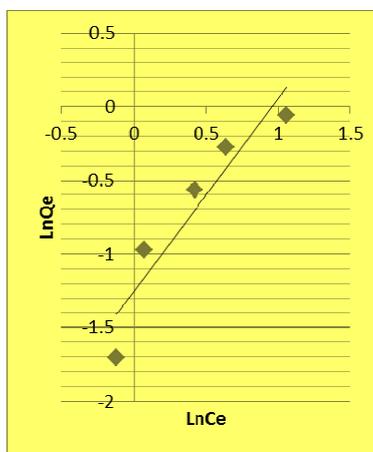


Fig. 8. Freundlich isotherm plot for Pb(II).

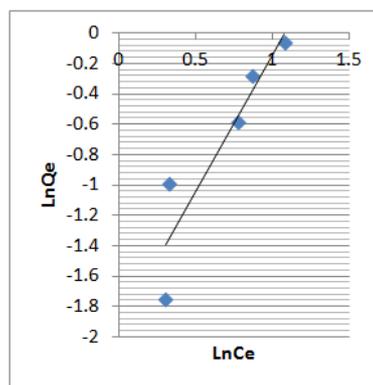


Fig. 9. Freundlich isotherm plot for Hg(II)

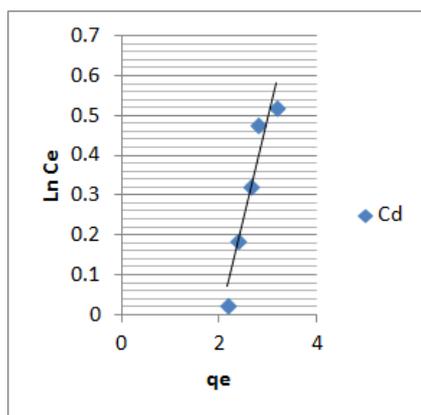


Fig. 10. Temkin isotherm plot for Cd(II)

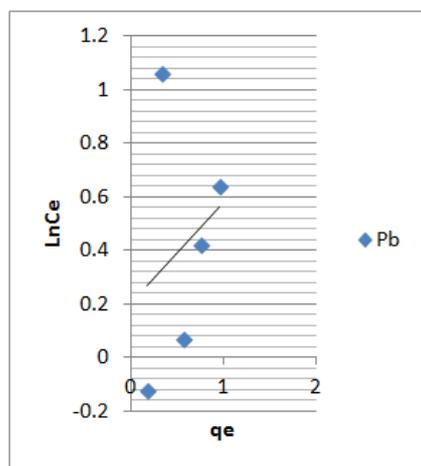


Fig. 11. Temkin isotherm plot for Pb(II)

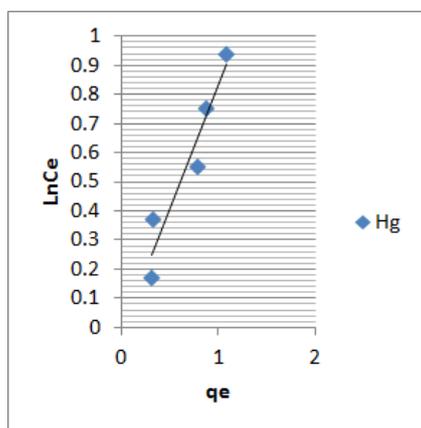


Fig. 12. Temkin isotherm plot for Hg(II)

3.4. The Effect of pH

One of the most important factors that affect the adsorption of metal ions is the pH of the solution, thus the pH affects both the adsorbent and the adsorbate chemistry in solution. The effect of pH on the adsorption of the heavy metal ions onto orange peels was studied at pH 2-8 for initial metal ion concentration of 40mg/l. It is observed that the percentage removal of the adsorption increased with increasing pH from 2-6 and then decreased. Also observed was that the Hg (II) ions removal increased between pH 2 and 4 but then

decreased from pH 6 to 8. At low pH, the sorbent surfaces are highly protonated with H⁺ ions, thus reducing available adsorption sites on which the equally positively charged Pb(II), Cd(II) and Hg(II) ions would have adsorbed to. Consequently, percentage adsorption is reduced. At moderate pH between 4 and 6, the concentration of the hydroxonium ions is fairly reduced, allowing for a considerable quantity of the metal ions. Reduction in percentage adsorption at basic pH of 8 may be as a result of formation of metallic hydroxide complexes at high pH.

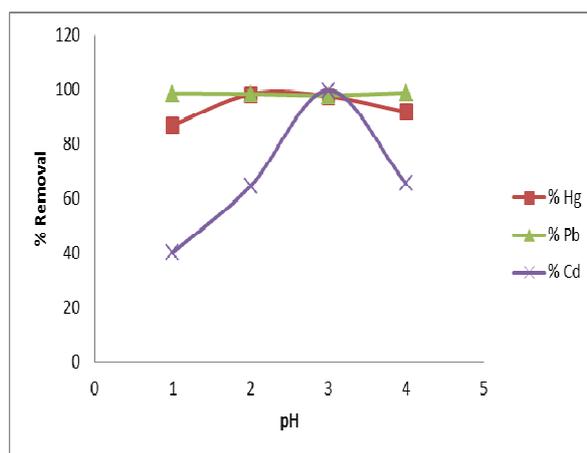


Fig. 13. A plot of pH against % removal of ions

3.5. Effect of Temperature

In designing adsorption systems, one should have an understanding of changes expected to occur and how fast they will take place. The fastness of the reaction can be calculated from the knowledge of kinetic studies, but the change in reaction that can be expected during the process requires the brief idea of thermodynamics parameters.

The thermodynamics parameters that must be considered to determine the process are enthalpy of adsorption (ΔH), free energy change (ΔG), and entropy change (ΔS) due to transfer of unit mole of solute from solution onto the solid-liquid interface.

The important thermodynamic function ΔH is very useful whenever there is a differential change in the system. The negative value of ΔH indicates exothermicity and the positive value of ΔH indicates endothermicity. The change in entropy, ΔS , indicates the randomness of the adsorption process. The parameter ΔG is used to determine the spontaneity and the feasibility of the adsorption process. The value of ΔG is calculated using the equation below [23].

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

Gibb's free energy is also given as

$$\Delta G = -RT\ln k_d \quad (10)$$

Where, k_d (distribution coefficient or equilibrium constant) is given as

$$K_d = q_e/c_e \quad (11)$$

Where q_e is the amount adsorbed per unit weight of the solid and C_e is the equilibrium concentration of solute in solution. Rearranging and making the required substitution yields

$$\ln k_d = \Delta S - \Delta H / RT \quad (12)$$

Table 3. Thermodynamics parameters for the adsorption

| Metal ions | ΔH (kJ/mol) | ΔS kJ/mol/s | ΔG (kJ/mol) | | |
|------------|------------------------|------------------------|---------------------|--------|--------|
| | | | 323K | 343K | 363K |
| Hg(II) | 11.07 | -49.22 | 17.00 | 17.99 | 18.97 |
| Pb(II) | 13.49 | -12.01 | 17.37 | 17.61 | 17.85 |
| Cd(II) | -14.92 | 37.49 | -27.03 | -27.78 | -28.53 |

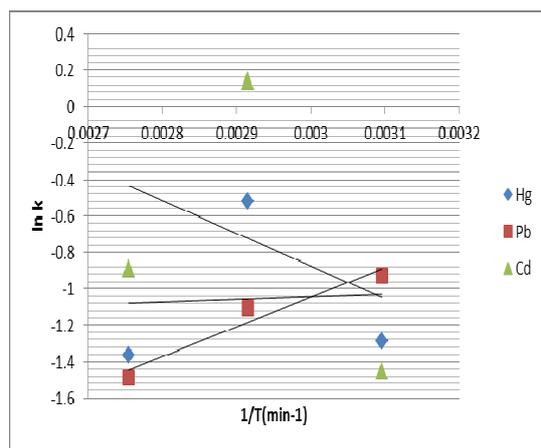


Fig. 14. Thermodynamics plot for adsorption

The values of ΔS and ΔH (table 3) were calculated from the intercept and slope from the plot of $\ln k_d$ versus $1/T$ (fig.14). The effect of temperature on the adsorption of Cd (II), Hg (II) and Pb(II) ions on orange peels was studied at three different temperatures; 323K, 343K and 363K. Adsorption of Hg (II) and Pb(II) ions are endothermic with change in enthalpies ΔH° of 11.07KJ/mol and 13.49KJ/mol respectively while that of Cd(II) ions is negative -14.92KJ/mol indicating that it is exothermic. It is observed from the table that changes in entropy ΔS° for Hg and Pb ions are negative: -49.22KJ/mol and -12.0154KJ/mol respectively. This indicates a decrease in the randomness of the adsorbed species, while that of Cd ions which is positive, 37.49J/mol indicating an increase in the degree of randomness.

The negative values obtained in ΔG° for Cd(II) ions indicate feasible and spontaneous adsorption while the positive values for Pb and Hg ions obtained from the thermodynamic calculations indicates a less feasible and non-spontaneous adsorption.

4. Conclusion

The present study showed that the surfaces of GOP were effective in the removal of Pb(II) Hg(II) and Cd(II) ions. The data were better fitted into the second order model. Adsorption with GOP is described by well-known isotherms and is also affected by pH.

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