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 Pub (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 Pub (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, electrodialysis, 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 2cm\(^{-1}\).

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 dissolution: 2.743g of Cd(NO\(_3\))\(_2\)·4H\(_2\)O, 1.60g of Pb(NO\(_3\))\(_2\) and 1.71g of Hg(NO\(_3\))\(_2\)·H\(_2\)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\(_2\)SO\(_4\) 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 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:

\[ q = \frac{(C_0 - C_e)v}{w} \]  

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 Pb(NO\(_3\))\(_2\) solution was measured into different beakers. The pH was adjusted from 2-8 using 0.5M H\(_2\)SO\(_4\) 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 Cd(NO\(_3\))\(_2\)·4H\(_2\)O and Hg(NO\(_3\))\(_2\)·H\(_2\)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 carboxyl groups were present on its surface. The broad vibration around 3080cm\(^{-1}\)-3500cm\(^{-1}\) is indicative of the presence of hydroxyl (–OH) and amino(-NH\(_2\)) 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):3022cm\(^{-1}\)-3775cm\(^{-1}\), Pb(II):3213cm\(^{-1}\)-3599cm\(^{-1}\) and Hg(II):3132cm\(^{-1}\)-3759cm\(^{-1}\). The peaks at 1582cm\(^{-1}\)-11767cm\(^{-1}\) 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)=1637cm\(^{-1}\) for Cd(II), Pb(II)=1664cm\(^{-1}\)-1882cm\(^{-1}\) and Hg(II)=1591cm\(^{-1}\)-1826cm\(^{-1}\). This confirmed that deprotonated carboxyl groups were involved in adsorption of Cd(II), Pb(II) and Hg(II) onto GOP. The band 1082cm\(^{-1}\) can be assigned to the stretching vibration of C–O. This band was clearly shifted after metal adsorption to higher wavelengths of 1088cm\(^{-1}\) for Pb(II) and lower wavelengths of 1001cm\(^{-1}\) for Hg(II) and 1005cm\(^{-1}\) 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:

\[
\ln (q_e^{(expt)} - q_t) = \ln q_e^{(theo)} - k_1 t
\]

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, \( q_e^{(expt)} \) is the amount of metal in (mg/g) adsorbed at equilibrium time obtained from experiments, \( q_e^{(theo)} \) is the amount of metal in (mg/g) adsorbed at equilibrium time obtained from theoretical model. Thus the rate constant \( k_1 \) and \( q_e^{(theo)} \) can be obtained from the slope and the intercept of the plot of \( \ln (q_e^{(theo)} - q_t) \) 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.
The pseudo second order kinetic model may be expressed by the equation[14]:

\[ \frac{t}{q} = \frac{1}{k_2q_e^{(theo)}^2} + \frac{1}{q_e^{(theo)}} \] (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 \( t \).

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

\[ q_e = \frac{q_mk_1c_e}{1+q_mk_1c_e} \] (4)

The reciprocal of the equation above yields

\[ \frac{1}{q_e} = \frac{1+q_mk_1c_e}{q_mk_1} + \frac{1}{q_m} \] (5)

A plot of \( 1/q_e \) against \( 1/C_e \) gives a straight line graph. The linear form of Langmuir isotherm equation is expressed as follows

\[ R_L = \frac{1}{1+K_L C_0} \] (6)

Where \( C_0 \) 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:

\[ \ln q_e = \ln k_f + \frac{1}{n} \ln C_e \] (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 \( \ln q_e \) versus \( \ln C_e \).

Temkin isotherm is represented by the Linear equation as follows;

\[ q_e = \frac{R_T}{b_T \ln C_e} + \frac{R_T}{b_T \ln K_T} \] (8)

Where, \( K_T \) and \( b \) are Temkin constants, \( R \) is universal gas constant (8.3143/K/mol) and \( T \) is temperature in Kelvin. A plot of \( q_e \)
vs. lnCe (figs 10-12) gives a slope and an intercept from which $b$ and $k_f$ 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.

<table>
<thead>
<tr>
<th>Model</th>
<th>Parameters</th>
<th>Hg(II)</th>
<th>Pb(II)</th>
<th>Cd(II)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$ (mg/g)</td>
<td>7.4619</td>
<td>5.7644</td>
<td>9.0365</td>
</tr>
<tr>
<td></td>
<td>$K_L$ (l/mg)</td>
<td>1</td>
<td>1</td>
<td>10.02</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.6959</td>
<td>0.835</td>
<td>0.643</td>
</tr>
<tr>
<td></td>
<td>$R_L$</td>
<td>0.342</td>
<td>0.561</td>
<td>0.267</td>
</tr>
<tr>
<td></td>
<td>$q_m$ (mg/g)</td>
<td>10.143</td>
<td>7.285</td>
<td>12.013</td>
</tr>
<tr>
<td>Freundlich</td>
<td>$N$</td>
<td>0.5596</td>
<td>0.7675</td>
<td>0.3592</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.8437</td>
<td>0.8822</td>
<td>0.7192</td>
</tr>
<tr>
<td>Temkin</td>
<td>$R^2$</td>
<td>0.9248</td>
<td>0.063</td>
<td>0.9128</td>
</tr>
</tbody>
</table>
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.

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].

\[ \Delta G = \Delta H - T \Delta S \]  

Gibb’s free energy is also given as

\[ \Delta G = -RT \ln K_d \]  

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

\[ K_d = \frac{q_e}{c_e} \]
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

$$\ln k_a = \Delta S - \Delta H / RT$$

(12)

| Table 3. Thermodynamics parameters for the adsorption |
|---|---|---|---|---|---|
| Metal ions | $\Delta H$ (kJ/mol) | $\Delta S$ (kJ/mol) | $\Delta G$ (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 |

The values of $\Delta S$ and $\Delta H$ (table 3) were calculated from the intercept and slope of the plot of $\ln k_a$ 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 $\Delta H^o$ 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 $\Delta S^o$ for Hg and Pb ions are negative: -49.22KJ/mol and -12.01KJ/mol respectively. This indicates a decrease in the randomness of the adsorbed species, while that of Cd ions which is positive, 37.49KJ/mol indicating an increase in the degree of randomness.

The negative values obtained in $\Delta G^o$ 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.

References


