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Calcium Ion Removal by $KMnO_4$ Modified Pineapple Leaf Waste Carbon Prepared from Waste of Pineapple Leaf Fiber Production Processing

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Abstract: Pineapple leaf fiber waste carbon, modified with 3% $KMnO_4$, was used for Ca^{2+} removal from aqueous solution. The effects of contact time, loading, water hardness, and isotherms on Ca^{2+} adsorption were studied. The results show that the Ca^{2+} ion removal by pineapple leaf fiber waste carbon could be improved by modification with $KMnO_4$. The adsorption would reach equilibrium state at about 60 min for a water source with hardness values of 40-200 mg/dm^3. Increases in total hardness (40 to 200 mg/dm^3) lead to a decrease in Ca^{2+} ion removal efficiency (90.05% to 37.65%) and an increase in Ca^{2+} ion adsorption capacity at equilibrium (4.37 mg/g to 8.95 mg/g). The Ca^{2+} removal efficiencies increase with increasing loading of modified waste carbon. The equilibrium data were fitted well by both the Langmuir isotherm and the Freundlich isotherm. For the Langmuir isotherm model, the values of the maximum Ca^{2+} adsorption capacity and Langmuir constant being 2.81 mg/g and 0.9262 dm^3/g, respectively. On the other hand for the Freundlich isotherm model, the K_F and n values are 1.374 dm$^{3(1/n)}$ mg$^{(1-1/n)}$/g and 4.671, respectively. These results indicate that modified pineapple fiber waste carbon is a material with high Ca^{2+} ion adsorption capacity, heterogeneity, and high affinity.

Keywords: Total hardness, calcium ion, magnesium ion, potassium permanganate, pineapple leaf fiber waste carbon

1 Introduction: Water hardness is mostly due to cations such as calcium and magnesium [1]. These metal ions are introduced into the environment through weathering of rock minerals and by anthropogenic activities, such as sewage discharge, transport, industrial effluents, and unplanned waste disposal [2]. Metal ions causing water hardness are responsible for two harmful effects, formation of deposits and destruction of soap. The deposits of water hardness linked cations generally occur due to the reaction with soap anions. This process produces soap scum, which dulls clothes and drastically reduces soap's cleaning efficiency [3]. It may also effect the taste of water [4]. These ions also induce scaling problems and serious failures in pipelines of boilers, heat exchangers, and electrical appliances such as washing machines, dishwashers, and steam irons [5]. The water treatment and softening technologies applied for drinking and industrial purpose have been widely investigated and are already commercialized. They include chemical precipitation, ion exchange process, reverse osmosis, electrodialysis [6], electrochemical oxidation process [7], nanofiltration, electromembrane systems such as electrodialysis, electrodialysis reversal, and electro-deionization reversal [5], biosoftening process (UASB-/CO_2 stripping unit) with biologically produced alkalinity for the formation of calcium carbonate [8], combined processes such as adsorption or coagulation with ultrafiltration or sand filtration processes [4]. The materials that have been used for hardness removal include resins for cation exchange [9], pine cones modified by citric acid [10], natural sand materials which are like zeolites

[11], mercerized cellulose and mercerized sugarcane bagasse grafted with EDTA dianhydride [12]. Quartz sand coated by MnO_2 and a biofilm containing micro-organisms, were also used as filter media for hardness removal [13] and they work by reacting quickly with manganese oxides in a manganese oxide treatment system [14]. The $KMnO_4$ modified sand showed a layer of compact, dense active substance and uniform texture, which is physically and chemically stable and had a greater capacity for metal ions [15].

This research studied $KMnO_4$ modified pineapple leaf fiber waste carbon for enhanced Ca^{2+} removal from aqueous solution. The effect of contact time, loading adsorbent, and hardness degrees for batch adsorption experiments were evaluated. The Langmuir isotherm and the Freundlich isotherm models for Ca^{2+} adsorption on these materials were also evaluated.

2. Materials and methods

2.1 $KMnO_4$ modified pineapple fiber waste carbon: $KMnO_4$ modified pineapple leaf fiber waste carbon obtained from Chemistry Department, Faculty of Science, Naresuan University, Phitsanulok, Thailand, was used for Ca^{2+} ion adsorption. It was prepared from pineapple leaf fiber waste carbonized at 500□C and modified with 3% $KMnO_4$. It was oven (SL 1375 SHEL LAB 1350 FX) dried at 105 °C for 3 h, and then used for Ca^{2+} adsorption experiments.
Preliminary study results of the 3% $KMnO_4$ modified pineapple leaf fiber waste carbon analysis showed that it consists of 59.56% C, 17.14% O, 6.82% Si, 8.65% K, and 7.82% Mn. It displayed a rough surface with cracks and a large number of small particles with high content of K and Mn. The functional groups on the surface of $KMnO_4$ modified waste carbon include H–O, C=O, C–O, C–Si–O, MnO_2, and Mn–OH. The BET surface area, pore volume, and average pore size of 3% $KMnO_4$ modified waste carbon are 167.4968 m^2/g, 0.08698 cm^3/g, and 2.0772 nm, respectively.

2.2 Calcium adsorption experiments: Batch calcium adsorption experiments were performed following the method of Pastrana-Martínez *et al.* [16]. Solutions with defined hardness values were prepared using distilled water and a calcium ion source. Total hardness, expressed as an equivalent content of calcium carbonate (mg/dm^3), was calculated according to equation (1).

$$CaCO_3\ (mg/dm^3) = 2.50\ [Ca^{2+};\ mg/dm^3] + 4.12\ [Mg^{2+};\ mg/dm^3] \qquad (1)$$

Water with total hardness of 40, 100, or 200 mg/dm^3 of $CaCO_3$ was prepared by using $CaCl_2$ (Merck, Germany) and $MgCl_2$ (Merck, Germany) dissolved in distilled water. Total hardness of 40, 100, and 200 mg/dm^3 $CaCO_3$ corresponds to soft, moderately hard, and hard waters, respectively. The pH of the synthetic and tap waters was between 8.0 and 8.7. Concentrations of Ca^{2+} and Mg^{2+} in the 40 mg/dm^3 total hardness sample were 9.7 and 3.9 mg/L respectively. For 100 mg/dm^3 total hardness samples the concentrations of Ca^{2+} and Mg^{2+} are 24.2 and 9.5 mg/dm^3 respectively, and for the 200 mg/dm^3 total hardness sample the concentrations of Ca^{2+} and Mg^{2+} are 48.0 and 19.1 mg/dm^3, respectively. Ca^{2+} concentration was determined by FAAS with 427.7 nm [17].

For Ca^{2+} adsorption experiments, $KMnO_4$ modified pineapple fiber waste carbon (0.1 g) was added to 50 cm^3 of Ca^{2+} solution (100 mg/dm^3 total hardness degree) in a conical flask. The suspension was shaken continuously at 120 rpm and a temperature of 32±2 ºC. Following the adsorption, the aqueous phase was separated by centrifugation at 4000 rpm for 10 min and the final concentration of Ca^{2+} ion in the solution was determined by FAAS (Varian SpectrAA 220, Australia) with air–acetylene and cathode on a Ca-hollow cathode lamp at 427.7 nm.

The adsorbed amount of Ca^{2+} was calculated by the difference in initial and final concentrations.
The optimum values for Ca^{2+} adsorption were determined at different conditions (e.g. contact time (0–180 min) and modified waste carbon loading (0.05–2.0 g)).

Final concentration (C_f) of Ca^{2+} was measured for the calculation of Ca^{2+} removal percentage as shown in the following equation (2) [18]:

$$Removal\% = ((C_o - C_f)/C_o) \times 100 \qquad (2)$$

where C_o is the initial Ca^{2+} ion concentration (mg/dm^3); C_f is the final Ca^{2+} ion concentration (mg/dm^3). The adsorption capacity (q_t, mg/g) at any time was calculated using a mass balance equation as shown in the following equation (3) [18]:

$$q_t = (C_o - C_f) \text{x} (V/W) \quad (3)$$

where V is the volume of the solution (dm^3); W is the mass of dry modified pineapple fiber waste carbon used (g).

2.3 Adsorption isotherms: All of the experimental adsorption data were fitted with both Langmuir and Freundlich equations.

The rearranged Langmuir equation is as follows [19]:

$$Q_e = (q_{max}K_L C_e)/(1 + K_L C_e) \quad (4)$$

where Q_e (mg/g) is the amount of Ca^{2+} ions adsorbed per unit mass of adsorbent, C_e (mg/dm^3) is the solute equilibrium concentration, q_{max} (mg/g) is the maximum adsorbate amount that forms a complete monolayer on the surface, and K_L (dm^3/mg) is the Langmuir constant related to adsorption heat.

The linear form of the above equation after rearrangement is:

$$C_e/Q_e = 1/q_{max}K_L + C_e/q_{max} \quad (5)$$

The constants q_{max} and K_L can be determined from the slope and intercept of plotting C_e/Q_e against C_e, respectively.

Freundlich model is used to estimate the adsorption intensity of $KMnO_4$ modified pineapple fiber waste carbon towards the Ca^{2+} ions and is expressed by the following equation: $Q_e = K_F Co^{(1/n)}$. This equation is conveniently used in its linear form as follows [19]:

$$\text{Log } Q_e = \text{Log } K_F + 1/n \log C_e \quad (6)$$

where Q_e and C_e have the same definitions as those in the Langmuir equation cited above. K_F and n are Freundlich constants related to adsorption capacity and heterogeneity factor, respectively. The constants K_F and n can be determined from the slope and intercept of plotting Log C_e against Log Q_e, respectively.

3. Results and discussion

3.1 Effect of $KMnO_4$ modification on Ca^{2+} adsorption efficiency: The effect of $KMnO_4$ modification on Ca^{2+} adsorption efficiency was evaluated by loading either 0.1 g pineapple leaf fiber waste carbon or 0.1 g of 3% $KMnO_4$ modified pineapple leaf fiber waste carbon in 50 cm^3 of 100 mg/dm^3 $CaCO_3$ total hardness water at pH 8.0-8.7 for 60 min contact time. The results show (Figure (1)) that the Ca^{2+} ions removal by pineapple leaf fiber waste carbon could be improved by modification with $KMnO_4$. The 3% $KMnO_4$ modified pineapple leaf fiber waste carbon exhibited greater Ca^{2+} ion absorption in comparison to pineapple leaf fiber waste carbon. The modified material could remove up to 78.71% of Ca^{2+} from the solution in comparison to only 42.6% removed by the unmodified waste carbon material. It is possible that the more pronounced Ca^{2+} ion removal capacity of 3% $KMnO_4$ modified pineapple leaf fiber waste carbon results from both the relatively high pH (8.0-8.7) and functional surface groups on the modified waste carbon (eg. carboxylate groups and Mn–OH groups), which favor increased Ca^{2+} ion adsorption. These effects result in more rapid accumulation of MnO_x colloids due to enhanced flocculation in response to specific adsorption of Ca^{2+} ions [20]. However, it can be seen that the efficiency is not high enough. This is because of the competing Mg^{2+} ions found in hard water.

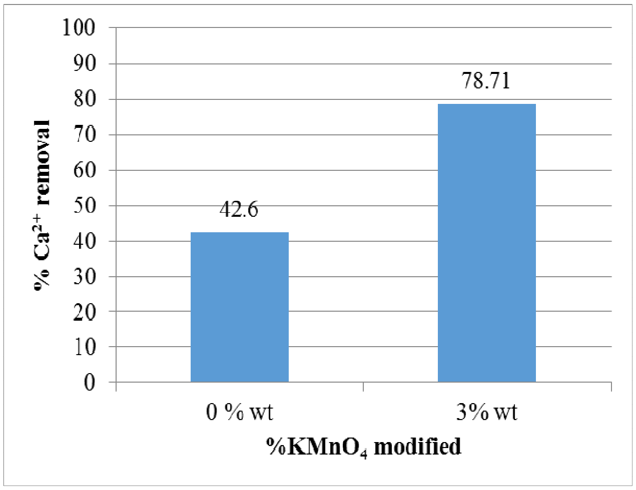

Figure (1): Comparison of Ca^{2+} removal by unmodified and 3%wt $KMnO_4$ modified pineapple fiber waste carbon materials.

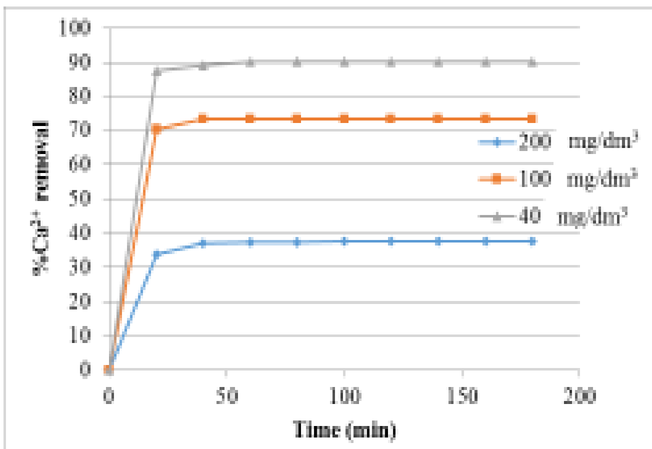

Figure (2): Effects of contact time and total hardness values on Ca^{2+} removal efficiency.

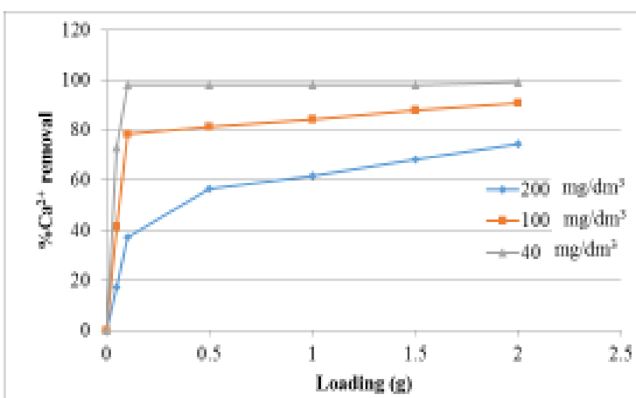

Figure (3): Effects of modified pineapple fiber waste carbon loading and total hardness on Ca^{2+} removal.

3.2 Effects of contact time and total hardness on Ca^{2+} adsorption efficiency: Experiments to determine the effect of contact time (0-180 min) and total hardness (40-200 mg/dm^3 of $CaCO_3$) on Ca^{2+} removal efficiency at pH 8.0-8.7 of 0.1 g of 3% $KMnO_4$ modified pineapple leaf fiber waste carbon in 50 cm^3 of water were carried out. Figure (2) shows that the Ca^{2+} adsorption rate is quite fast, and reaches equilibrium state after about 60 min for all total hardness values. It can be seen that adsorption efficiency was improved by increasing the contact time. The initial rapid adsorption may be due to the availability of initial large number of vacant sites of adsorbent. Afterwards, the filling of vacant sites becomes more difficult due to repulsive forces between Ca^{2+} ions adsorbed on the modified waste carbon surface and Ca^{2+} ions in solution **[21]**. Furthermore, increasing the contact time increases the contact between the adsorbent and the metal ions, which increases the availability of interaction between the active functional groups in the adsorbent and the metal ions. Consequently, the amounts of metal ions adsorbed by functional groups increase, which increases the metal ions uptakes **[22]**. Furthermore, increasing the total hardness value leads to a decrease in Ca^{2+} ion removal efficiency and an increase in Ca^{2+} ion adsorption capacity at equilibrium. The Ca^{2+} adsorption capacities of modified waste carbon are 4.37 mg Ca^{2+}/g for 40 mg/dm^3 total hardness, 8.86 mg Ca^{2+}/g for 100 mg/dm^3 total hardness, and 8.95 mg Ca^{2+}/g for 200 mg/dm^3 total hardness, which is attributed to an increase of the concentration gradient increasing the driving force for adsorption from the solution to the adsorbent surface. This in turn leads to increase in adsorbate amount per unit of adsorbent **[23]**. In the other words, the increase in initial concentration of Ca^{2+} ions enriches its interaction with the adsorbent **[24]**, which in turn enhances the adsorption process. While Ca^{2+} ion removal efficiencies are 90.05%, 73.26%, and 37.65% for 40, 100, and 200 mg/dm^3 total hardness, respectively. This could be explained by the empty sites on the surface of modified waste carbon being occupied immediately and leading to increased difference in concentration between the bulk liquid and initial ion concentration resulting in decrease of removal efficiency due to the increase in Ca^{2+} ion concentration at constant modified waste carbon loading [23].

3.3 Effects of modified carbon loading and total hardness degrees on Ca^{2+} adsorption efficiency: Figure (3) shows the Ca^{2+} removal efficiencies with 0.05–2.0 g loading of 3% $KMnO_4$ modified pineapple fiber waste carbon and 40-200 mg/dm^3 $CaCO_3$ total hardness values for 50 cm^3 at pH 8.0-8.7 and 60 min contact time. It shows that the Ca^{2+} removal efficiency decreases with increasing total hardness from 40 to 200 mg/dm^3 for the same adsorbent loading. This could be explained in the same way as in the experiment determining the effect of contact time and total hardness. Furthermore, the Ca^{2+} removal efficiency for 40 mg/dm^3 hardness value reaches 98.2 % with only 0.1 g of 3% $KMnO_4$ modified pineapple fiber waste carbon loading and is then constant with further additions of the adsorbent. It could be concluded that only 0.1 g of 3% $KMnO_4$ modified pineapple fiber waste carbon (0.2 %wt/V) is sufficient for virtually complete Ca^{2+} ion adsorption at 40 mg/dm^3 total hardness value. The Ca^{2+} removal efficiency for 100 mg/dm^3 and 200 mg/dm^3 total hardness increase with increasing adsorbent loading from 0.05 to 2.0 g. This increase of the Ca^{2+} ion removal efficiency for increasing modified waste carbon loading indicates the accessibility of a larger number of sorption sites at higher dosage to adsorb Ca^{2+} ions [23].

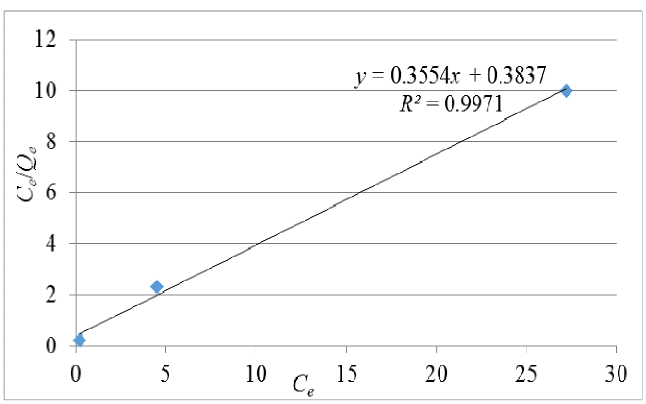

Figure (4): Langmuir isotherm plots for Ca^{2+} ion adsorption by 3% $KMnO_4$ modified pineapple fiber waste carbon.

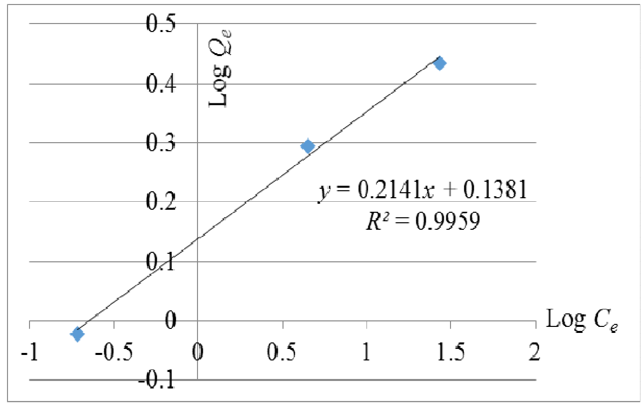

Figure (5): Freundlich isotherm plot for Ca^{2+} ion adsorption by 3% $KMnO_4$ modified pineapple fiber waste carbon.

3.4 Ca^{2+} ion adsorption isotherm models: Ca^{2+} ion adsorption isotherm studies were carried out with a loading of 0.5 g of 3% $KMnO_4$ modified pineapple fiber waste carbon in 50 cm^3 samples containing 9.7, 24.2, and 48.0 mg/dm^3 Ca^{2+} ion concentration, at pH 8.0-8.7 and a 60 min contact time. Langmuir isotherm and Freundlich isotherm are used to correlate the Ca^{2+} ion adsorption equilibrium data. It was seen that the equilibrium data were fitted well by both the Langmuir model (Figure (4)) and the Freundlich model (Figure (5)). The R^2 values of the linear forms of these isotherm curves are nearly equivalent with R^2 values of 0.9971 and 0.9959 for Langmuir isotherm and Freundlich isotherm, respectively. These results indicate that the surface of the 3% $KMnO_4$ modified pineapple fiber waste carbon contains most likely heterogeneous moieties, which were uniformly distributed on the surface [23]. Furthermore, this study revealed that the Ca^{2+} ion adsorption occurs on heterogeneous surface of 3% $KMnO_4$ modified pineapple fiber waste carbon, but take place only in a monolayer without interaction between Ca^{2+} ions in the 56.2-247 mg/dm^3 concentration range. Furthermore, there is no transmigration of the modified waste carbon [25]. According to the Langmuir equation, the values of the maximum Ca^{2+} adsorption capacity and Langmuir constant were 2.81 mg/g and 0.9262 dm^3/g, respectively. The dimensionless parameter (R_L), which is calculated from the value of C_0 and K_L using the relationship $R_L = 1/(1+ K_LC_0)$, has a value of 0.0515-0.2118 falling in the range $0<R_L<1$. Therefore, 3%

$KMnO_4$ modified pineapple fiber waste carbon appears to be highly favorable for Ca^{2+} ion adsorption under these experimental conditions [26]. For the Freundlich model, the K_F and n values are 1.3744 $dm^{3(1/n)}$ $mg^{(1-1/n)}/g$ and 4.671, respectively. These indicate that modified pineapple fiber waste carbon exhibits high Ca^{2+} ion adsorption capacity with heterogeneity [19] and high affinity, which is confirmed from the Freundlich factor (n) values within the range 1–10 [23].

4. Conclusions: The 3% $KMnO_4$ modified pineapple leaf fiber waste carbon has high potential for Ca^{2+} removal from aqueous solution. It could remove Ca^{2+} ions with almost twice the efficiency of the unmodified waste carbon material. The contact time needs to reach equilibrium state is only 60 min for samples with total hardness of 40-200 mg/dm^3 using 0.05-2.0 g loading of the adsorbent. This is attributed to the functional surface groups and texture of the modified waste carbon material. The Ca^{2+} ion removal efficiency decreases (90.05% to 37.65%), while Ca^{2+} ion adsorption capacity is increases (4.37 mg/g to 8.95 mg/g) with increasing total hardness (40 mg/dm^3 to 200 mg/dm^3) for constant modified waste carbon loading. Both the Langmuir isotherm and the Freundlich isotherm models fit well the experimental data, which indicates that the Ca^{2+} ion adsorption occurs on the heterogeneous surface of 3% $KMnO_4$ modified pineapple fiber waste carbon, but take place only in a monolayer without interaction between Ca^{2+} ion in the 9.7-48.0 mg/dm^3 concentration range (or 40-200 mg/dm^3 total hardness value). The parameter values from both isotherms eg. the values of the maximum Ca^{2+} adsorption capacity (2.81 mg/g), Langmuir constant (0.9262 dm^3/g), dimensionless parameter (0.0515-0.2118), K_F (1.374 $dm^{3\ (1/n)}$ $mg^{(1-1/n)}/g$), and n values (4.671), indicate that the modified pineapple fiber waste carbon possesses high Ca^{2+} ion adsorption capacity with heterogeneity and high affinity giving it highly favorable properties.

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