Adsorption behavior of Pb(II) in aqueous solution using coffee husk-based activated carbon modified by nitric acid

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ABSTRACT: *Activated carbon (AC) was prepared from coffee husk and modified by nitric acid for effective lead ions removal from aqueous solution. The as-prepared samples have uniform particles size, developed surface area and contain acidic surface functional groups. Nitric acid modification showed a pronounced effect on improving Pb(II) adsorption capacity. The Freundlich isotherm model and pseudo second-order kinetic model could best describe the adsorption of Pb(II) onto AC-Nitric. Thermodynamics parameters proved the spontaneous, physic and endothermic nature of the adsorption of Pb(II) onto AC-Nitric.*

Keywords -Activated carbon, Adsorption, Coffee Husk, Lead Ions

I.   INTRODUCTION

The pollution of heavy metals, especially lead ions, gave serious impact on the health of humans and other living organisms even at low concentrations [1]. The main sources of human exposure to lead are including: metallurgy, metal plating, mining, industrial tanning, acid battery manufacturing... [2]. Although numerous techniques for the removal of metal ions have been established, like chemical precipitation, electrochemical precipitation, evaporation, ion exchange, membrane separation ... [3], sorption is consider an effective method with the advantage of low cost, high removal efficiency, economical feasibility and ease of processing. However, the main drawback of this method is that the commercially adsorbent is considerate expensive, lead to the high cost of wastewater treatment. To overcome this problem, naturally abundant resources or agricultural by-products such as activated carbon, chitosan, lignite, kaolin, diatomite, limestone, zeolite, bentonite... [4-6] have been studied excessively. Vietnam ranks second in coffee exporting, which means that the low economic value by-products are also generated. With high carbon content, the coffee husk is considered as potential activated carbon precursor. Previous studies have demonstrated that by modifying to enhance the oxygen containing functional groups, pore size, ion exchange capacity or hydrophilic surface properties, heavy metal adsorption capacity of the activated can be markedly improved [7].

This paper presents the research results of surface modification of activated carbon prepared from coffee husk by nitric acid for the enhancement of lead ions adsorption in aqueous solution.

II.   EXPERIMENTAL

2.1. Preparation and surface modification of activated carbon

The coffee husk was carbonized at a temperature of $450^{o}C$ for 1.5 hour. After that, it was impregnated with KOH at the char/base ratio of 1:3 (wt.).The impregnated sample was activated at $750^{o}C$ for 60 min then washed separately with 2M HCl and warm distilled water until pH 6-7. Thereafter, the as-prepared sample was dried, labeled as AC-CF and stored in a desiccator ready for use.

Surface modification was achieved by weighing 5.0 g AC-CF and placing it in an Erlenmeyer containing 50 mL 2M HNO_3 for 12 hours. After that, the sample was washed thoroughly with distilled water until constant pH. The obtained modified activated carbon was dried, marked as AC-Nitric and placed in a desiccator ready for use.

2.2. Characterization of activated carbon

The surface morphology features of raw and modified activated carbon were observed by Field Emission Scanning Electron Microscope S4800–Hitachi.

The oxygenated surface groups were determined by Boehm titration method [8]. Amounts of the various acidic functional groups were calculated by assuming that NaOH reacts with all groups, Na_2CO_3 reacts with carboxylic and lactonic groups, and NaHCO3 only reacts with carboxylic group. Experimentally, 0.5 g activated carbon sample was added to 50 mL of each 0.1 M aqueous solution ($NaHCO_3$, Na_2CO_3, NaOH) and the mixtures were allowed to stand for 72 h at room temperature. The filtered solution was titrated with 0.1 M HCl to determine the acidic group contents. For basic groups, the same procedure was applied with 50 mL 0.1 M HCl solution and titrated with standardized 0.1 M NaOH.

The specific surface area and the pore texture of activated carbon was charaterized by nitrogen adsorption/desorption at 77 K, using a Micromeritics TriStar 3020. The specific surface area (S_{BET}) was calculated by applying the BET equation to the adsorption data [9]. The microporous surface area (S_{mic}) and external surface area (S_{ext}), as well as the micropore volume (V_{mic}) were evaluated by the t-plot method [10]. The mesopore volume (V_{mes}) was estimated by the Barrett–Joyner–Halenda (BJH) method [11]. The total pore volume (V_{tot}) was evaluated by sum of microporous and mesoporous volumes. The pore size distribution of AC samples was calculated using density functional theory (DFT) [12] with the assuming that the pore of the sample has slit shape.

2.3. Adsorption experiment

A stock solution of Pb(II) (0.3 g L^{-1}) was prepared by dissolving $Pb(NO_3)_2$ (Sigma–Aldrich) in double distilled water. All diluted Pb(II) solutions were obtained as required by further dilution with double distilled water. The concentrations of Pb(II) before and after adsorption were determined by AAS.

In this study, all the adsorption experiment was performed at natural pH of solutions (≈ 6.5). Adsorption isotherms were conducted by placing a determined weight of AC in 100 mL Erlenmeyer flasks containing 50 mL of Pb(II) solution in initial concentrations ranging from 45 to 105 mg L^{-1}. The flasks were kept in an isothermal shaker (120 rpm) at different temperature (10, 20, 30 and 40°C) for 15 h. Then AC was separated from the solution by filtration prior to analysis. Kinetics experiments were carried out using 62.84 mg L^{-1} Pb(II) solution and 0.2 g AC in a 250 mL flask which was kept in a temperature-controlled water bath ($10 \div 40^o$C) and the aqueous solution–adsorbent mixtures were stirred at 150 rpm. At preset time intervals, 2 mL samples were pipetted out, filtered and the residual Pb(II) concentrations were measured.

The percentage of Pb(II) adsorption on AC, α (%); the amount of adsorption at time t, q_t(mg g^{-1}) and the adsorption capacity at equilibrium, q_e (mg L^{-1}), were calculated using the formulas:

$$\alpha = \frac{C_e}{C_o} \times 100\% \qquad (1)$$

$$q_t = \frac{(C_0 - C_t)V}{m} \qquad (2)$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad (3)$$

where C_0, C_t and C_e (mg L^{-1}) are liquid-phase concentrations of Pb(II) at initial, time t and equilibrium, respectively. V (L) is the volume of the solution and m (g) is the mass of dry AC used.

III.   RESULTS AND DISCUSSIONS

3.1. Characterization of activated carbon

The surface morphology of activated carbon samples observed by SEM are shown in Fig.1. AC-CF and AC-Nitric exhibited a nearly spherical shape with diameter in the range of $20 \div 50$ nm. Acid modification appeared to have no obvious effect on the particle size of the AC.

The presence of acidic and basic groups on the surface of activated carbon, before and after the acid treatment, evaluated by Boehm method is showed in Table I. The results reveal a remarkable increase in the amount of acidic groups (from 2.633 to 3.372 mmol g^{-1}) while decrease in the amount of basic groups (from 0.305 to 0.017 mmol g^{-1}) after modification. This could be explained by the reaction between nitric acid and basic functional groups chromene or pyrone to form acidic functional groups by heterocyclic opening [13]. Besides, it could be due to the fact that nitric acid can neutralize and even destroy basic groups [14].

The N_2 adsorption–desorption isotherms at 77 K of the ACs under study were presented in Fig.2. All the isotherms belong to type I in the IUPAC classification [15]. There was an important uptake at low relative pressures, characteristic of microporous materials (pore width< 2 nm). However, the knee of the isotherms is quite wide with no clear plateau attained, indicating the presence of larger micropores and mesopores ($2 \leq$ pore width≤ 50 nm) [15].
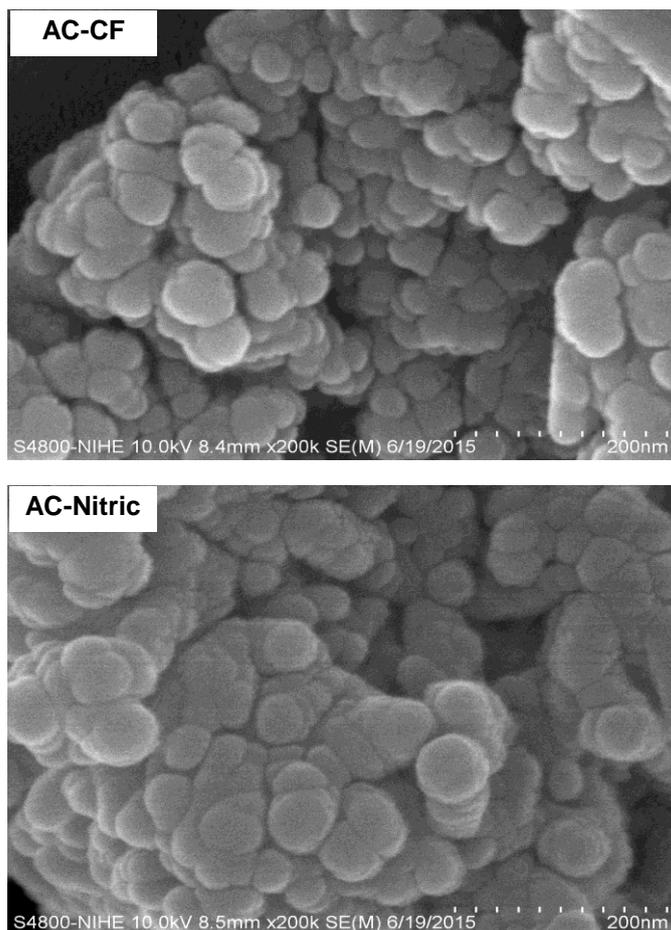
Figure 1: SEM images of activated carbon samples

Table I: Number of surface groups obtained from Boehm titration

Sample	Surface groups concentration (mmol g^{-1})				
	Carboxylic	*Lactonic*	*Phenolic*	*Total acidity*	*Total basicity*
AC-CF	1.300	0.916	0.416	2.633	0.305
AC-Nitric	1.678	1.183	0.511	3.372	0.017
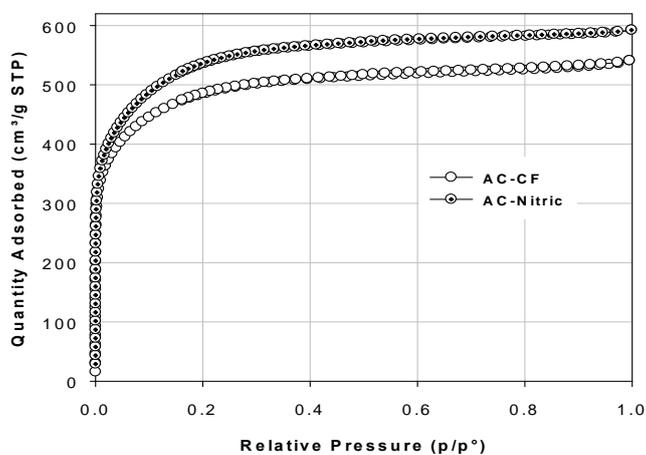
Figure 2: N_2 adsorption - desorption isotherms at 77K of AC-CF and AC-Nitric

From the N_2 adsorption–desorption isotherms, it is possible to obtain the specific surface areas and the pore texture of the ACs. Results summarized in Table II shows that AC derived from coffee husk by KOH activation process a developed BET surface area and a high pore volume, mostly contain of micropore. The nitric acid modification resulted in the increase of BET surface area (from 1773 to 1961 m^2 g^{-1}) which is due to the increase of micropore surface area and micropore volume (from 1730 to 1914 m^2 g^{-1} and from 0.7692 to 0.8543 cm^3 g^{-1}, respectively).

Table II: Textural properties of the as-prepared ACs obtained by N_2 adsorption-desorption at 77K

Sample	S_{BET} m^2g^{-1}	S_{mic} m^2g^{-1}	S_{ext} m^2g^{-1}	V_{mic} cm^3g^{-1}	V_{ext} cm^3g^{-1}	V_{tot} cm^3g^{-1}
AC-CF	1773	1730	43	0.7692	0.0674	0.8366
AC-Nitric	1961	1914	47	0.8543	0.0721	0.9264
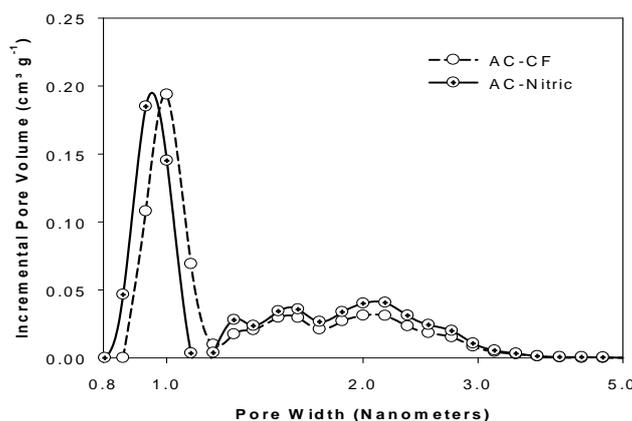
Figure 3: Pore size distribution of activated carbon before and after nitric acid modification

The pore size distribution of ACs obtained by DFT reveals that pore width of all the AC samples is less than 5.0 nm, therefore, Fig.3 only illustrates in the size range of 0.8 ÷ 5.0 nm. It can be noticed that the ACs mostly containing micropore with a majority of ultra-micropore (pore width ≤ 1.0 nm). The nitric acid modification caused mostly the increase of micropores. The obtained results are in accordance with the specific surface area and pore texture given before.

3.2. Adsorption of Pb(II) in aqueous solution

The adsorption isotherms of Pb(II) at 30°C onto AC-CF and AC-Nitric are showed in Fig.4. It can be clearly seen from Fig.4 that the adsorption capacity of AC is almost double after nitric acid modification. This might be due to the developed specific surface area of AC-Nitric sample. Furthermore, the amount of acidic functional groups onto AC-Nitric surface is surpass that of AC-CF, this could be contributed to the increase in adsorption capacity of Pb(II) due to the ability to bind with heavy metals of carboxyl, phenol, quinine...[16]. Due to the high adsorption capacity after nitric acid treatment, AC-Nitric is used as adsorbent for further study.
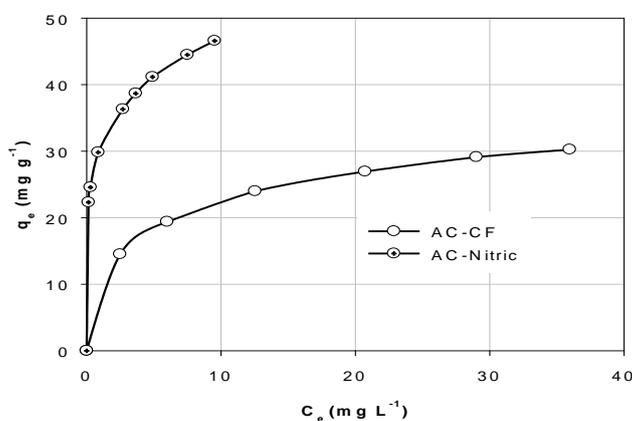
Figure 4: Adsorption of Pb(II) at 30°C onto activated carbon before and after nitric acid modification V = 50 mL; m = 100 mg

3.2.1. Adsorption equilibrium of Pb(II) onto AC-Nitric
a) Effect of adsorbent dose

The effect of adsorbent dose of AC-Nitric was investigated using 62.12 mg L^{-1} Pb(II) solution at 30°C to determine the optimum mass of adsorbent. The results presented in Fig.5 showed that as the amount of AC-Nitric increased from 1.0 to 2.0 g L^{-1}, the % removal also increase from 93.1 to 98.6%. Nevertheless, further increasing in adsorbent dose to 3.5 g L^{-1}, the % removal only increased slightly to 99.7%. This could be explained by the change in surface area and the number of active site of activated carbon. When adsorbent mass less than 2.0 g L^{-1}, free Pb(II) ions are considerably abundant, the increase of adsorbent leads to the increase of surface area and active site, which in turn increase the adsorption efficiency. However, at certain amount of adsorbent, the quantity of Pb(II) ions adsorbed on AC and the amount of free ions is in equilibrium. Therefore increasing the AC dose cannot change the % removal [17]. Along with the increase of AC dose, the adsorption capacity of AC decline due to the unsaturated adsorption site in the adsorption process. Therefore, the optimum adsorbent dose of 2.0 g L^{-1} (i.e. 100 mg AC in 50 mL solution) has been chosen for further study.
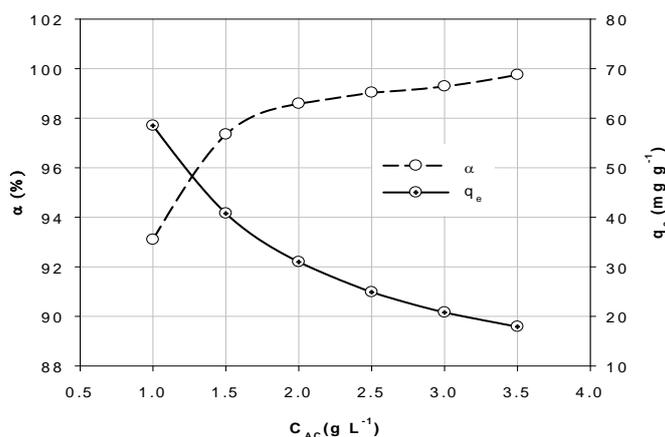
Figure 5: Effect of adsorbent dose (T = 30°C, C_o = 62.12 mg L^{-1})

b) Equilibrium adsorption

Adsorption capacities of lead ions adsorbed against the equilibrium concentrations of Pb(II) in aqueous solution at 30°C are plotted in Fig.6. Adsorption capacity increase as the increasing of equilibrium concentration of Pb(II), proving the unsaturated adsorption nature of Pb(II) in the investigate concentration range.

Table III: Isotherms and the parameters involved in the different equilibrium adsorption isotherms [18]

Isotherm expression		*Parameter*
Langmuir:	$q_e = \dfrac{q_m . K_L C_e}{1 + K_L C_e}$	q_m: maximum adsorption capacity K_L: Langmuir constant
Freundlich:	$q_e = K_F . C_e^{1/n}$	K_F: Freundich constant $1/n$: heterogeneity factor ($0 < 1/n < 1$)
Sips:	$q_e = \dfrac{q_m \left(K_s C_e \right)^{m_s}}{1 + \left(K_s C_e \right)^{m_s}}$	q_m: maximum adsorption capacity (mg g^{-1}) K_S: Sips constant m_s: Sips model exponent
Toth:	$q_e = \dfrac{q_m . C_e}{\left(K_{Th} + C_e^t \right)^{1/t}}$	q_m: maximum adsorption capacity K_{Th}: Toth constant $1/t$: Toth model exponent

Four most frequently employed adsorption isotherm models (two parameter isotherms: Langmuir and Freundlich, as well as three parameter isotherms: Sips and Toth) were adopted to describe the experiment data obtained and displayed in Table III. The parameters of these isotherm equations were calculated using a nonlinear regression by minimizing the values of the hybrid fractional error function (HYBRID) given in equation (4) [18]. The best fit isotherm was selected based on this model and the HYBRID that produced minimum value of the average relative error (ARE) given in equation (5).

$$HYBRID = \frac{100}{N-p} \sum_{i=1}^{N} \left[\frac{\left(q_{e,calc} - q_{e,meas} \right)^2}{q_{e,meas}} \right]_i \qquad (4)$$

$$ARE(\%) = \frac{100}{N} \sum_{i=1}^{N} \left| \left(\frac{q_{e,calc} - q_{e,meas}}{q_{e,meas}} \right)_i \right| \qquad (5)$$

where: $q_{e,meas}^i$, $q_{e,calc}^i$ are the equilibrium capacity (mg g^{-1}) calculated from the applied model and obtained from the experimental data; N is the number of measured points, p is the number of parameters.

The results of nonlinear regression of Langmuir, Freundlich, Sips and Toth adsorption isotherms are showed in Fig.6 and summary in Table IV. The Freundlich isotherm exhibited lowest ARE value (0.85%) compared to Langmuir, Sips and Toth models, therefore considered to be a best fit to the experimental data. Besides, it can be easily seen from Fig.6 that the Freundlich fitting is nearest to the experimental data. Therefore, the Feundlich isotherm model is the best-fitting isotherm in this experiment condition.

Table IV: The values of HYBRID and ARE obtained by using different isotherm models

Model	HYBRID	ARE (%)
Langmuir	11.382	8.54
Freundlich	**1.133**	**0.85**
Sips	3.751	2.81
Toth	6.359	3.97
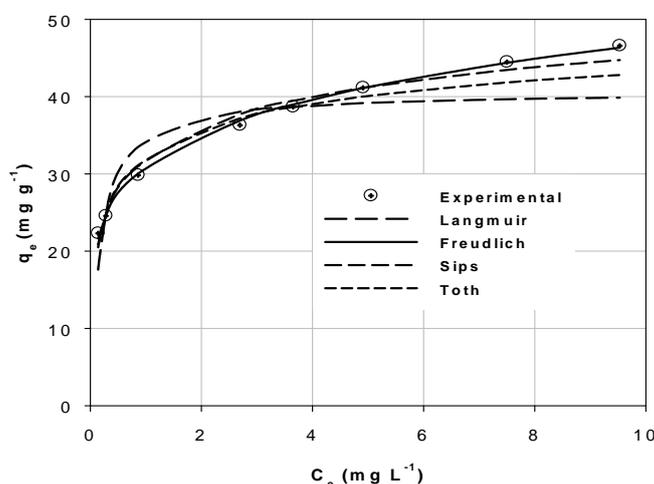
Figure 6: Adsorption isotherms of Pb(II) on AC-Nitric at 30°C. The line curves were calculated using four models listed in Table III
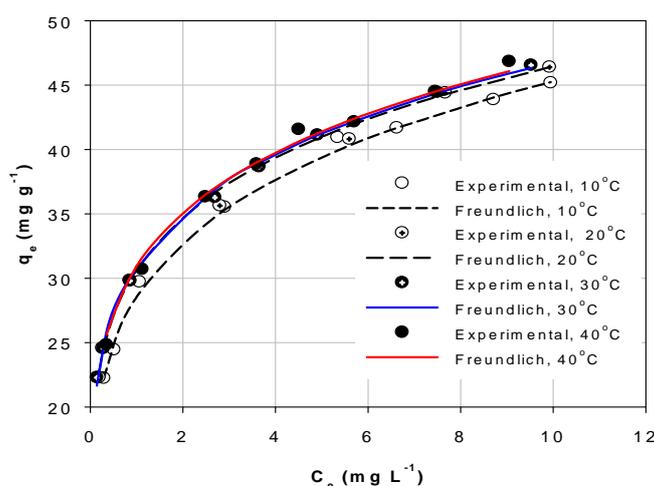
Figure 7: Adsorption isotherms of Pb(II) on AC-Nitric at different temperature.
The curves were calculated using the Freundlich equation

Effect of temperature on the adsorption of Pb(II) was studied in the range of 10 ÷ 40°C. The experimental data in Fig.7 showed that the adsorption capacity is slightly increased at higher temperature.

Table V: Freundlich isotherm parameters of the adsorption of Pb(II) onto AC-Nitric at different temperatures

T(ºC)	K_F	n	HYBRID	ARE(%)
10	28.508	4.98	1.401	1.05
20	30.698	5.56	2.121	1.51
30	30.870	5.55	1.133	0.85
40	30.962	5.54	1.904	1.43

Freundlich isotherm parameters as well as HYBRID and ARE values obtained at four temperatures are showed in Table V. As it can be seen from the Table V, the Freundlich constant K_F increase from 28.508 to 30.962 as temperature increase from 10 to 40ºC, which means the adsorption capacities are enhanced accordingly.

3.2.2. Adsorption kinetic of Pb(II) onto AC-Nitric

a) Effect of contact time

Fig.8 show the adsorption capacities of Pb(II) onto AC-Nitric at 4 different temperatures as a function of time, q_t. The results show that q_t is increased rapidly within the first 10 minutes, then slowing down and finally approaching equilibrium after 180 min. Nevertheless, to ensure the equilibrium is established, the total contact time used is 15 h.
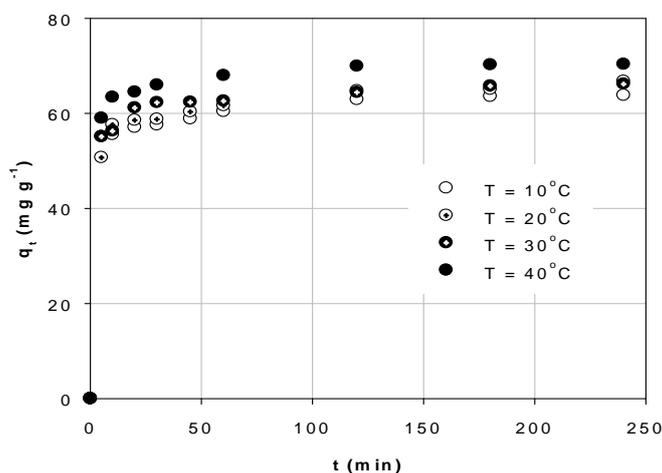
Figure 8: The adsorption capacities of Pb(II) onto AC-Nitric at 4 different temperatures
(C_o = 62,12 mg/L, m = 200 mg, V = 250 mL)

b) Kinetic adsorption equation

Kinetic of the adsorption of Pb(II) onto AC-Nitric was investigated using two common equations, pseudo first-order (Lagergren's equation) [19] and pseudo second-order kinetic models [18]. The linear expression can be illustrated as equation (6) and (7) as followed:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \qquad (6)$$

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \qquad (7)$$

where: k_1 (min⁻¹) and k_2 (g mmol⁻¹ min⁻¹) are the pseudo first-order and pseudo second-order rate constants, respectively.

The values of k_1 and k_2 are calculated from the slope of equation (6) and (7) by linear regression. The relevance of each equation is evaluated through the correlation coefficient R^2 and the difference between the experimentally determined values of adsorption capacities, q_e^{meas}, and the calculated values, q_e^{calc}.

Results calculated based on above equation for the adsorption of Pb(II) onto AC-Nitric at 30ºC were plotted in Fig.9. The rate constant and the calculated values of adsorption capacities at four temperatures are summarized in Table VI. For the pseudo second-order rate equation, the correlation coefficient is approximately 1 and q_e^{calc} is almost equal to q_e^{meas}. Therefore, the adsorption of Pb(II) onto AC-Nitric in aqueous solution follows pseudo-second-order rate equation. This result is in accordance with the adsorption of Pb(II) ions onto pine cone activated carbon [20].
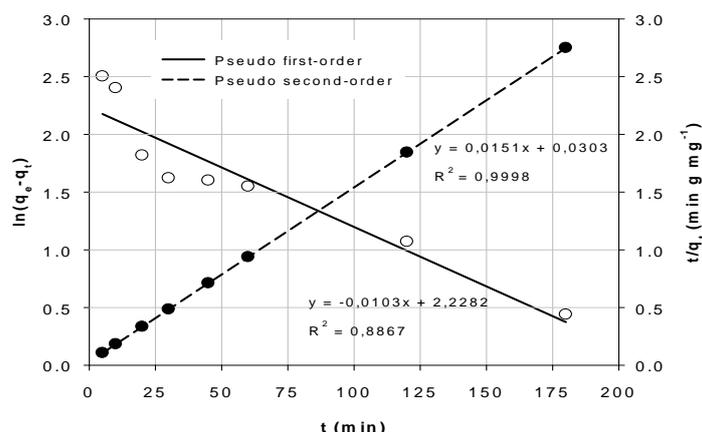
Figure 9: Pb(II) uptake by AC-Nitric at 30°C according to pseudo first-order and pseudo second-order kinetic model (C$_o$ = 62,12 mgL^{-1}, m = 200 mg, V = 250 mL)

Table VI: Calculated and experimental qe values and the pseudo first and second-order rate constants for the adsorption of Pb(II) by AC-Nitric at different temperatures

T (^{o}C)	q$_{e,meas}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		k$_1$ ×10^2 (min^{-1})	q$_{e,cal}$ (mg g^{-1})	R^2	k$_2$×10^3 (g mmol^{-1} min^{-1})	q$_{e,cal}$ (mg g^{-1})	R^2
10	66.5123	8.20	11.1674	0.9654	5.76	64.5161	0.9998
20	66.7375	1.21	11.4926	0.9184	6.14	65.3595	0.9992
30	67.3123	1.03	9.2831	0.8867	7.53	66.2252	0.9998
40	70.2126	5.83	25.7157	0.9109	8.35	70.9220	0.9999
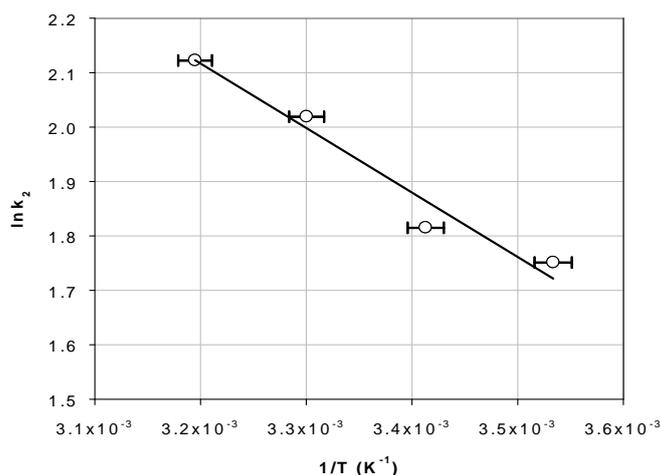
Figure 10: Plots of lnk$_2$ against 1/T

Fig.10 shows the linear plots of lnk$_2$ against 1/T. Activation energy E$_a$ calculated from the slope of that linear is ≈ 9.849 kJ mol^{-1}. Therefore, it is inferred that the adsorption of Pb(II) onto AC-Nitric in aqueous solution is most likely physisorption process.

3.2.3. Thermodynamic parameters

Thermodynamic parameters of Gibbs free energy change, $\Delta G°$, enthalpy change, $\Delta H°$, and entropy change, $\Delta S°$, for the adsorption of Pb(II) onto AC-Nitric are calculated using the following equations:

$$\Delta G^0 = -RT \ln K_0 \qquad (9)$$

$$\ln K_0 = -\frac{\Delta H^0}{R} \cdot \frac{1}{T} + \frac{\Delta S^0}{R} \qquad (10)$$

where K_o is the equilibrium constant.

In order to ensure the K_o in Eq (9) and (10) is dimensionless, in this study, K_o was calculated based on the equation proposed by Slobodan K. Milonjic [21]:

$$K_o = \frac{q_e}{C_e} \times 1000 \qquad (11)$$

C_e was chosen between 0.5 and 10 mg L^{-1}; q_e was calculated according to the Freundlich isotherm with the parameters listed in Table V. From this, $\Delta G°$ was calculated.
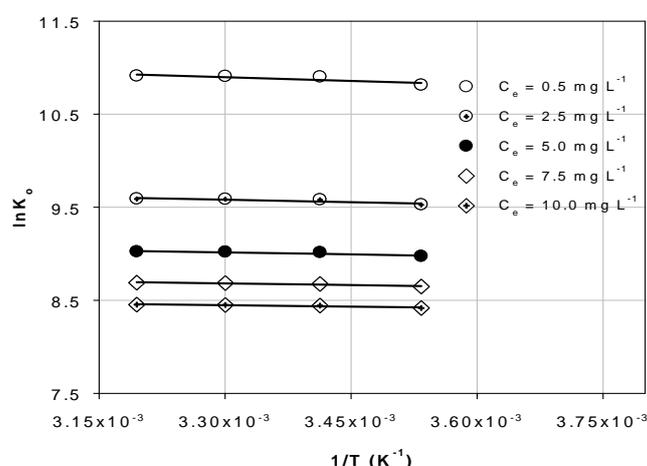
Figure 11: Plots of $\ln K_o$ versus 1/T for the adsorption of Pb(II) onto AC-Nitric

Table VII: Thermodynamic parameters for adsorption of Pb(II) onto AC-Nitric

C_e (mg L^{-1})	ΔG^o (kJ mol^{-1})				ΔH^o (kJ mol^{-1})	ΔS^o (J mol^{-1} K^{-1})
	10^oC	20^oC	30^oC	40^oC		
0.5	-25.44	-25.65	-25.66	-25.67	2.22	97.91
2.5	-22.41	-22.54	-22.56	-22.56	1.48	84.55
5.0	-21.11	-21.20	-21.22	-21.23	1.17	78.80
7.5	-20.35	-20.42	-20.44	-20.44	0.98	75.42
10.0	-19.81	-19.87	-19.88	-19.89	0.85	73.03

The ΔH^o and ΔS^o values can be determined from the plot of $\ln K_o$ versus 1/T. Plots of $\ln K_o$ versus 1/T at five chosen C_e are shown in Fig.11, and the thermodynamic parameters calculated accordingly for Pb(II) adsorption onto AC-Nitric are summarized in Table VII. As can be seen from Table VII, the negative value of $\Delta G°$ confirms the feasibility of the process and the spontaneous nature of adsorption with a high preference for Pb(II) to sorb onto AC-Nitric. The positive value of ΔH^o and ΔS^o suggesting endothermic nature, and there was increased randomness at the solid/solution interface during the sorption of Pb(II) onto AC. A positive $\Delta H°$ was also reported for the adsorption of Pb(II) onto sawdust based activated carbon [22]. The value of ΔS^o is positive due to the breakage of the hydration shell of Pb(II) ions during adsorption onto AC.

It is evident from the Table VII that ΔG^o was less negative at high C_e, suggesting that the spontaneous process decreased with the increase of C_e. The elevation of C_e also resulted in the decrease in ΔH^o and ΔS^o. The two last parameters decreasing from 2.22 to 0.85 kJ mol^{-1} and from 97.91 to 73.03 J mol^{-1} K^{-1} respectively while C_e increased from 0.5 to 10 mg L^{-1}. This could be explained as follows: a high C_e increased the amount of Pb(II) adsorbed, hence, the number of active AC sites decreased significantly leading to a lower degree of spontaneity.

The high amount of Pb(II) on the AC surface also resulted in the increase of repulsive forces between the adsorbed Pb(II), which in turn decreased the degree of disorder which led to the decrease in entropy. In all case, the ΔH^o is much lower than 70 kJ mol^{-1} indicated the physical nature of the adsorption of Pb(II) onto AC-Nitric. These results correspond well with and confirm the conclusion from the adsorption kinetic studies.

IV.   CONCLUSION

The adsorption of Pb(II) from aqueous solution onto activated carbons prepared from coffee husk by KOH activation and modified by nitric acid was studied. The nitric acid modification resulted in the increasing specific surface area, pore volume and acidic functional groups, which in turn improving Pb(II) adsorption capacity more than twice compare to the unmodified one. The adsorption of Pb(II) onto the modified activated carbon follows the pseudo-second-order kinetic and Freundlich isotherm model. The adsorption process on AC-Nitric is endothermic and physisorption with activation energy 9.849 kJ mol^{-1} The obtained results revealed the potential use of nitric modification of coffee base-activated carbon for the removal of Pb(II) from aqueous solutions.

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