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REMOVAL OF LEAD IONS FROM AQUEOUS SOLUTION ON TO LOW COST ACTIVATED CARBON AS A SOURCE OF WOODS SAWDUST WASTE

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Abstract

Wood saw dust residual was employed as precursor to synthesize activated carbon (AC) as it is cheap and easily available. The synthetization process was carried out by performing carbonization followed by acid treatment. The synthesized activated carbon from saw dust (ACSD)S was then employed as adsorbent to remove lead ions from aqueous solutions. Both physio-chemical characterization, and kinetic and isothermal equilibrium studies were conducted. It was observed that the acid functional groups at the surface of ACSD promote the cation exchange efficiency. The measured pH_{PZC} was 4.2 and the adsorptive mechanism was well described by SSS second-order kinetics model. The experimental results were good resented by the Langmuir's isotherm model. The highest sorption uptake was 170 mg/g at pH of 5.0. The results show that the prepared ACSD is a cost-effective and promising adsorbent for removing Pb^{2+} from aqueous solution.

Key words : Wood sawdust; Lead; Activated carbon; Adsorption isotherm; Equilibrium S kinetics.

Introduction

Water Sis essential for the survivability of humans and other life forms. Since a few decades ago, water has been severely polluted by heavy metals generated from industrial and human activities. These heavy metals are highly mobile and non-biodegradable which would stay in living tissues (Jeevanantham *et al.,* 2019).

It is known that lead is a longstanding contaminant which would impose risk to the health of humans and aquatic organisms. As reported by the US Ecological Protection Agency's, the lead level in consumption water should not exceed 0.05 Sppm, which raise the public health concerns (Mohod and Dhote 2013). Therefore, appropriate strategies should be devised to address the pollution problem due to lead. For eliminating Pb^{2+} in particular, methods' such as membrane processes, monolithic scaffolds, bio-sorption, ion exchange, coagulation and flocculation, complexation, etc. have been proposed (Bernardo *et al.,* 2013; Hernández-Martínez *et al.,* 2017; Qin *et al.,* 2016). These technologies are expensive and they are not readily implementable in developing countries. In order to address this problem, adsorption using natural materials is attractive as it is cost-effective, simple and environmentally favorable (Crini *et al.,* 2018).

In practice, materials such as biopolymers, natural clay, industrial wastes, fly ash, metal oxides, zeolite, microorganisms, etc. have been used as adsorbents (Crini *et al.,* 2019). Recently, adsorbent such as activated carbon (AC) hiss been found to be very attractive for treating wastewater (e.g. removal of toxic metal ions) thanks to its promising adsorption characteristics, high porosity, design simplicity and abundance in nature ((Al-Shehri *et al.,* 2019). However, the fabrication cost of AC is quite high; thus, techniques of producing AC from cheap and renewable sources such as wood charcoal, charcoal, algae etc. have been explored (Crini *et al.,* 2018; Hagemann *et al.,* 2018; Maneerung *et al.,* 2016; Pal *et al.,* 2017). However, these sources are expensive and show low efficiency.

Hence, it is necessary to develop an adsorbent that is cost-effective by identifying new precursors for

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producing AC. Some examples are agricultural lignocelluloses wastes (Kosheleva *et al.,* 2019), which can be used to prepare wood-based AC that is ecofriendly. AC of high surface area and porosity can be fabricated via a carbonisation and activation of the carbon-containing residue. As reported, for adsorbing species of positive charge, the oxygenated functional groups of oxygen can be applied on the adsorbents as they act as ion exchangers (Acevedo *et al.,* 2015; Bohli and Ouederni 2016).

In the current work, the feasibility of using AC made from Iraqi wood sawdust (ACSD)S in removing lead (Pb^{2+}) from aqueous solution is studied. ACSD is an easily available by-product from the Iraqi wood furniture industry. To date, few attempts have been made to use ACSD for treating wastewater, particularly in the removal of Pb(II) ion. In order to synthesize ACSD, pyrolysis (or carbonization) was firstly performed. Then, oxidation was approved out using nitric Acid. Subsequently, the effectiveness of using ACSD in removing the Pb^{2+} ionsS from aqueous result was determined. Finally, the equilibrium removal behavior of ACSD was examined. It is anticipated that this work is useful for environmental engineers in elucidating the mechanism of lead adsorption using ACSD.

Materials and Methods

Activates Carbon Training

The woods sawdust waste remainder which was acquired forms a sawmills in Baghdadis was dries at 105 °C for 1 day and cleaned using distilled water. Then, the impurities were removed from the sample via filtration. The sample was then dried-up at 110 °C for 1 day and kept in a desiccator. Then, the sample was grinded and sieved to obtain particles of size ranging from 1 - 2 mm. These particles were further dried for another 24 hr. Carbonization was then performed at 700 °C for 2 hr on the dried sawdust sample under inert condition, *i.e.* by using flowing N_2 at 150 mL/min. This procedure was performed in a cylindrical incinerator where heating rate was 10 C/min. fixed at 10 °C/miss. Scaling ways then performed on the carbonized samples. These samples were then washed using 0.2 MS HNO_{3S} for 3 hr. Finally, the samples were cleaned using distilled water (Jazuli 2015).

Resolve of pH at the opinion of zeroes charge (pH_{PZC})SS

The value of pH_{PZC} was attained byes performing pH titration (Nasiruddin Khan and Sarwar 2007). Adsorbent of mass 0.15 g was mixed with 50 mL aqueous solutions (at different pH conditions) contained in Erlenmeyer flasks. The initial pH was adjusted by stirring 0.1 M NaOH or HCl solutions at 120 rpm and 25°C for 24 h. The pH of each solution was then measured and the constant pH value appeared in the pH_{final} against $pH_{initial}$ plot was taken as pH_{pzc}.

Resolve of surfaces actives site

The Boehm's titration method was used to identify the surface functional groups on ACSD (Boehm 1994). This process was performed by mixing 0.2 g of adsorbent with various 50 mL solutions, *i.e.* 0.1MHCl, NaOHS, Na_2CO_3 and $NaHCO_3$, contained in different flasks. A total of 10 mL aliquots were titrates with 0.1 M SNaOH or S HCl thrice. The amount of the attached acid groups was calculated based on the following assumptions: (a) carboxyl clusters', lactones and phenolic can be neutralized sings NaOH; (b) carboxylic collections and lactones can be neutralized by Na_2CO_3; and (c) carboxylic clusters are neutralized using $NaHCO_3$. Nevertheless, the quantity of basic sites was determined from the amount of HCl reacting with the material.

Groundwork of Leads Solutions'

The solutions were of lead concentration 1000 mg/ SL prepared by mixing Pb $(NO_3)_{2S}$ with deionizes water. Pb $(NO_3)_2$ was selected by way of the hostage ion as it is little in tendency in forming metal developments. These lead solutions were before diluting accordingly to obtain solutions of concentration ranging from 100 mg/L to 500 mg/L. preliminary pH of S solution can be controlled by adding HCl or NaOH.

Bunch Equilibriums Revisions

Adsorptions measurements of ACSD (q_e, mgs/g) determined using calculation (1). Upon filtering's suspension, primary andS ending concentrations were determined accordingly.

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where m is the adsorbent amount (g) and V is the solution volume (L). The initial and final concentrations are denoted as C_o and C_e, respectively (Chen and Bai 2013). In the current work, the adsorption experiments were repeated twice, and the maximum deviation of 5 % was found. Many previous studies showed that the removal of lead ions in acidic environment was inefficient owing to the interaction with H_3O^{+S} ions. Also, the existence of $OH^{"}$ in the alkaline solution would motivate the reaction of lead ions with water to form $PbS(OH)^+$ and $PbS(OH)_2$ (Gerente *et al.,* 2007; Hendricks 2005; Mashangwa 2016). Therefore, all adsorption experiments were performed its pH S5.00 by shaky 0.1 gM adsorbents writhes 50 mL of occupied solution's of prescribed concentration's. Shaking was conducted using a mechanical shaker operating at 2000 (rpm)S. During the experimentation, pHS values of solutions were ensured be consistent. Lastly, filtration was performed on the supernatant liquids. The metal concentration in wasS then stately by the nuclear preoccupation's spectrophotometer.

Bunch Kinetics Trainings

PseudoS-FirstS-OrderS Kinetics Typical

Frequency continuous adsorptions k_1 (h^{-1}) was calculated,the pseuds first-orders model, by plotting lnn (q_{eS} - q_{tS}) against t (Bohli *et al.*, 2015) for different initial concentrations:

$$\ln n(q_e - q_t)ss = \ln q_e s - K_1 ts$$

Here, q_e, sq_t quantities offs adsorbed ssPb^{+2} (mg/gm)s at the symmetry and at random time s*et*, respectively.

Pseudos'-Seconds-OrdersKinetics Prototypical

Pseudo second-order model built on the steadiness adsorptions can be written as:

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_2} t$$

where k_{2S} (gm/mg. hr) sis the proportion constants for the seconds-orders adsorptions (Demirbas *et al.*, 2004).

Adsorptions Isotherms Simulations

Herein, the adsorption records of ACSD was investigated by means of the Langmuir's and Freundlichs adsorptions reproductions.

Langmuir's Isotherms

Langmuir isotherms prototypical cans be carved as:

$$\frac{C_e}{q_e}s = \frac{1}{Q_{max\,K_L ss}} + \left(\frac{1}{Q_{max\,ss}}\right) ss C_e$$

where C_e sis the equilibriums concentrations of the adsorbents (mgs/Ls), $q_{e\,s}$is the total of adsorbents adsorbed per element mass' of adsorbents (mgs/gm), sQ_{max} is the all-out adsorbent-phase concentrations (mgs/ls) and K_{Ls} is the Langmuir continuous.

Freundlich Isotherm

Freundlich classical can be written mathematically as:

$$\log q_{se} = \ln K_{sF} + \frac{1}{n} \ln s\, C_{e ss}$$

sassq_e andC_e are thes adsorptions capability (mgs/gm) and attentiveness of the adsorb ate at equilibrium, respectively. K_{Fs} ,s n are Freundlichs quantities (Matouq *et al.*, 2015).

Results

Physicals–chemicals physiognomies

The specific appearances of adsorbents, *i.e.* moisture content, bulk density, surface area, residue content and solubility in water were analyzed and reported in table 1.

Estimation of pH_{PZC}

Argument where an adsorbent has zero potential charge on its surface is defined as the point of zero charges (pH_{PZC}). As reported in Fig. 1, pH_{PZC} is approximately 4.0. At pH > 4.0, the surface charge of AC is predominantly negative and vice-versa. At the point of zero charge, pH ~ 7.0 (Aroua *et al.*, 2008; Bernardo *et al.*, 2013; Shim *et al.*, 2001). This phenomenon, however, is not observed in the current work. The measured pH_{PZC} is lower due to interaction between the H^{+S} ions and superficial of ACSDSS. Next to pH = 5, the adsorption's of Pb^{+2S} is quite effective due to the negatively charged surface thanks to the protonated surface functional groups (Legrouri *et al.*, 2017).

Determination' of superficial practical collections

Adsorption's possessions and the surface charge of AC are dependent at surface functional groups. As reported in Table 1, the ACSD exhibits highly acidic amphoteric character due to the dominant carboxylic groups whereby its percentage is additional than 70%s of this acid sets. In other words, the lead ionss can be detached efficiently.

Adsorptions Kinetics

Slab 2 reports the standards of rate constant for the

Table 1: Characteristic properties of as-prepared activated carbon (ACSD).

Property	Value
Moisture (%)	4.68
Ash (%)	2.26
pH (1%solution)	7.18
Bulk density (g/l)	0.76
Water soluble components (inorganic matter) (%)	20.18
Insoluble components (organic matter) (%)	78.43
Surface area (m^2/g)	978.66
Total pore volume (cm^3/g)	0.89
Total acid sites (mmol/g)	6.73
Phenolic groups (mmol/g)	0.58
Carboxylic groups (mmol/g)	4.92
Lactonic groups (mmol/g)	1.05
Total basic sites (mmol/g)	0.98

Table 2: Experimental values of kinetics model's constants.

Model	Equation	Parameters	Values
Pseudo-First-Order	$ln(q_e-q_t)= lnq_e-k^1t$	R^2 K_1	0.9130.037
Pseudo-Second-Order	$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	R^2 K_2	0.9990.014

Table 3: Linearized equations of studied isotherm models.

Model	Equation	Parameters	Values
Freundlich	$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e$	R^2 K_f n	0.87626.972.83
Langmuir	$\frac{C_e}{q_e} = \frac{1}{K_l Q_{\max}} + \left(\frac{1}{Q_{\max}}\right) C_e$	q_m K_L R^2	170.240.1640.998

Table 4: Comparison of the maximum adsorption uptake (q_m) with previous studies.

Adsorbent	q_m (mg/g)	Reference
ACSD	170.24	The present work
Granular activated carbon	14.0	(Fernando *et al.* 2015)
Peanut husks carbon	109.31	(Zohre *et al.* 2010)
Activated carbon	123	(Suresh *et al.* 2011)
Date pits carbon	50.25	(Liu *et al.* 2014)
Cotton stalk	147.06	(Deng *et al.* 2011)
Graphene/magnetite composite	43.08	(Ai *et al.* 2011)
Rice husk ash	99.83	(Norzilah *et al.* 2011)

pseudos' firsts-orders besides the seconds-orders models. As seen from Fig. 2, the R^2 value of the pseudo second order model is ~ 1, thereby approving the model reliability. At the beginning, the metal elimination rate is high due to the availability of active adsorptive sites. Furthermore, it is noticed the symmetry time reductions with respect to the initial lead concentration.

Isotherm studies

From Fig. 3, the adsorption of Pb(II) ions on ACSD follows the Freundlich and Langmuir adsorption models. Nevertheless, the fitting of Langmuir model is more convincing (see Fig. 3b) upon analyzing the reversion constants reported in table 3. This shows that monolayer adsorption occurs at the adsorbent surface that contains a several identical sites. The values of K_L and Q_{max} are 0.164 L/g and 170.24s mg/gm, correspondingly.

Table 4 compares the adsorption capacities of several sorbents (for lead removal) obtained from previous studies. As seen, the adsorption uptake of the current ACSD is promising and it could serve as a good adsorbent for removing lead metal from contaminated effluents.

Discussion

Present two-steps' process consisting of carbonization and acid dealing adjustment has been found to effective in transforming wood saw dust to bios-adsorbents form removing Pb^{2+} from aqueous solution. Using HNO_3 (acid treatment purpose), the amount of acidic carboxylic groups can be increased to facilitate the adsorption process and to lower the pH_{pzc} to ~ 4.2. The pseudo second-order kinetic models have been used to fit the experimental kinetics data. In particular, higher linear correlation coefficient has been attained by using the Langmuir isotherm model. The highest adsorption capacity of ACSD is ~170 mg /g and it could serve as a potential alternative for removing lead ions from contaminated effluents.

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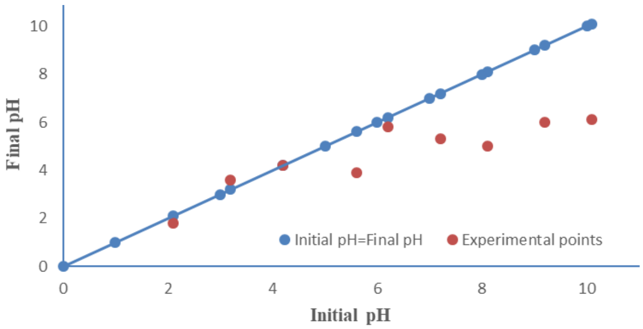

Fig. 1: Curve of pH at point of zero charge (pH_{Pzc}).

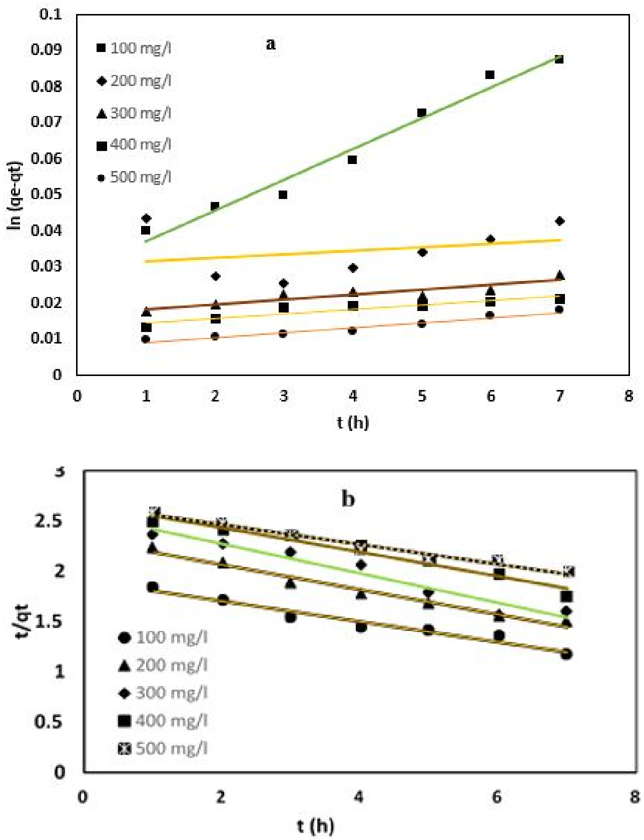

Fig. 2: Linearization of Pb(II) adsorption kinetics onto ACSD for different initial concentrations represented by (a) Pseudo-first and (b) Pseudo-second order models.

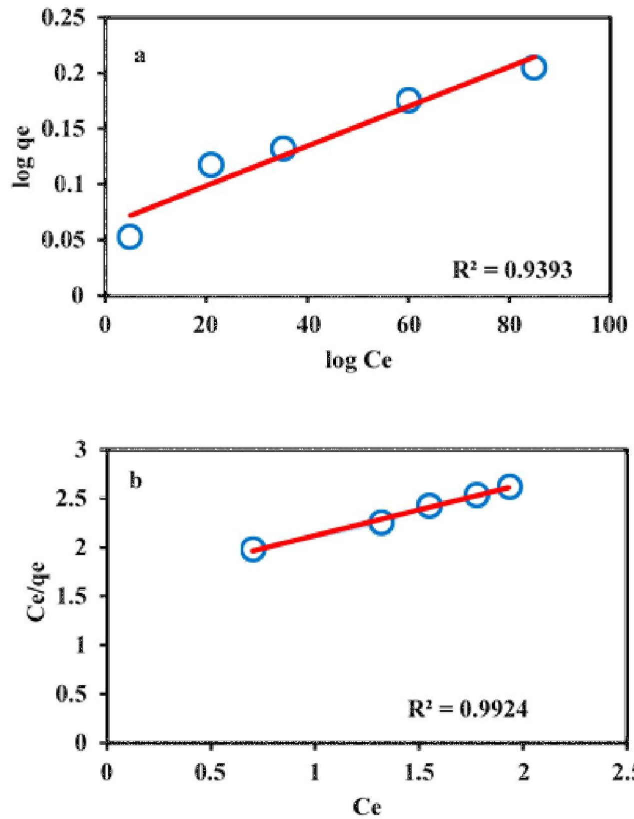

Fig. 3: Experimental isotherm plots for the adsorption of Pb(II) onto ACSD represented by: (a) Langmuir and (b) Freundlich isotherm models.

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