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Removal of Lead (II) Metal Ions from Aqueous Solutions Using Modified Kennan's Sugarcane Bagasse Activated Carbon Combined with Natural Zeolite

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Abstract

This work presents a systematic comparative evaluation of sugarcane bagasse-derived activated carbons from Kennana Sugar Company—Sudan, chemically activated using KOH and H_3PO_4 and composited with natural zeolite, for the adsorption of Pb(II) ions from aqueous media. The adsorption process exhibited optimal performance under mildly acidic conditions (pH 5.0 - 6.0). Equilibrium data were analyzed using Langmuir and Freundlich isotherm models, with both models showing strong agreement with experimental results; however, the Langmuir model provided the most accurate representation, indicating predominantly monolayer adsorption. Freundlich analysis further suggested that Pb(II) uptake on both composites is governed mainly by a physisorption mechanism. The adsorbents demonstrated high affinity toward Pb(II) ions, with maximum monolayer adsorption capacities of 588.24 mg g^{-1} for AC (KSCB)KOH-zeolite and 161.29 mg g^{-1} for AC (KSCB)H_3PO_4-zeolite, as determined from Langmuir isotherms. Corresponding Langmuir affinity constants (K_L) were 138.77 and 92.39, respectively, confirming stronger Pb(II) -adsorbent interactions for the KOH-activated composite. Overall, the carbonized AC (KSCB)KOH-natural zeolite composite exhibited markedly enhanced adsorption performance compared to its H_3PO_4-activated counterpart, underscoring its potential as a cost-effective and sustainable material for efficient lead remediation in water treatment applications.

Subject Areas

Physical Chemistry

Keywords

Kennan's Sugarcane Baggase (KSB), Activated Carbon, Natural Zeolite, Lead Adsorption, Isotherm Modeling, Water Treatment

1. Introduction

Access to safe drinking water is fundamental to human life and should not pose significant health risks [1]. Although certain heavy metals are essential in trace amounts, their elevated concentrations can result in serious adverse health effects [2]. Both natural processes and anthropogenic activities represent major pathways for the release of heavy metals into the environment, leading to persistent contamination of surface water, groundwater, and seawater. Additional contamination of drinking water may arise from metal leaching within water distribution systems (WDS). While desalination processes can remove a portion of heavy metals from seawater, desalinated drinking water may still contain various metals due to post-treatment stabilization, blending with treated groundwater, and corrosion or leaching from distribution pipelines [3] [4]. Among the heavy metals of concern in drinking water, Pb, Hg, As, Cd, Cr, Cu, and Ni are particularly hazardous owing to their relatively high concentrations and toxicity [5] [6]. Lead contamination primarily originates from industrial activities such as tanning and leather processing, pigment and catalyst production, fungicides, ceramics, glass manufacturing, photography, electroplating, corrosion control, and other manufacturing sectors [7] [8].

Several techniques have been developed for the removal of undesirable metal ions from contaminated water, including adsorption, ion exchange, chemical precipitation [9], membrane separation [10], electrocoagulation [11], nanoparticle-based treatment [12], and dialysis or electrodialysis [13]. Among these methods, adsorption has emerged as the most widely applied approach due to its operational simplicity, design flexibility [14], cost-effectiveness, and environmentally friendly nature [15]. Moreover, adsorption offers high removal efficiency and versatility, enabling the treatment of a wide range of pollutants in water and wastewater systems. Adsorption is a surface phenomenon in which dissolved or gaseous species accumulate at the interface of a solid or liquid adsorbent, forming a molecular or atomic layer on the adsorbent surface [16].

The objective of this study was to synthesize microporous activated carbon from sugarcane bagasse via chemical activation using KOH and H_3PO_4, followed by compositing with commercial natural zeolite in varying ratios to develop an efficient adsorbent for Pb(II) removal from aqueous solutions. The effects of key operational parameters—including solution pH, adsorbent dosage, initial metal ion concentration, and contact time—on the removal efficiency of AC(KSCB)KOH and AC(KSCB) H_3PO_4 were systematically investigated. In addition, the porous characteristics of the synthesized materials were examined to identify the optimal composite for effective lead ion recovery from aqueous media.

2. Martial and Methods

Pb(II) stock solutions were prepared by dissolving appropriate amounts of lead nitrate salt, $Pb(NO_3)_2{\cdot}4H_2O$ (Fluka, Germany), in distilled water. The initial Pb(II) concentrations used in the adsorption equilibrium experiments ranged from 10 to 150 mg L^{-1}.

Kennan's sugarcane bagasse (KSCB), collected from Kennana Sugar Company in White Nile State, Sudan, was used as the precursor material for activated carbon preparation and is hereafter referred to as AC(KSCB). Prior to use, the raw bagasse was repeatedly washed with hot distilled water to remove surface impurities, followed by drying at 105˚C for one week. Natural zeolite (clinoptilolite) was supplied by Fluka (Germany). According to the supplier's specifications, the zeolite consisted primarily of clinoptilolite (>80%), with minor amounts of heulandite and mordenite, and trace quantities of quartz, sanidine, and biotite.

All chemical reagents used in this study were of analytical grade and supplied by Merck and Fluka (Germany), and were used without further purification.

2.1. Preparation of Activated Carbon

After complete drying, the prepared activated carbon AC(KSCB) was crushed and grinded in a ball mill. Grinded sample was sieved to obtain homogeneous particles of uniform < 90 - 125 μm. Two 100g AC(KSCB) samples were impregnated with KOH and H_3PO_4 for 72 h each in a ratio of 1:1.5˚C at 50˚C to achieve well saturation of the chemical into their interior. After saturation, the samples were dried for 72 hrs. at 105˚C. The solid residues were cooled to room temperature, then thoroughly washed with double distilled water followed by 0.10 M Hydrochloric Acid (HCl) or 0.10 M Sodium Hydroxide (NaOH) to remove or eliminate the chemical residual, until the rinsed water pH values were neutral. The adsorbents prepared were denoted as AC(KSCB) H_3PO_4 and AC(KSCB) KOH throughout the work. Carbonization the temperature 500˚C - 600˚C and the time 1.5 - 2 hours once the target temperature is reached and shown in Figure 1.

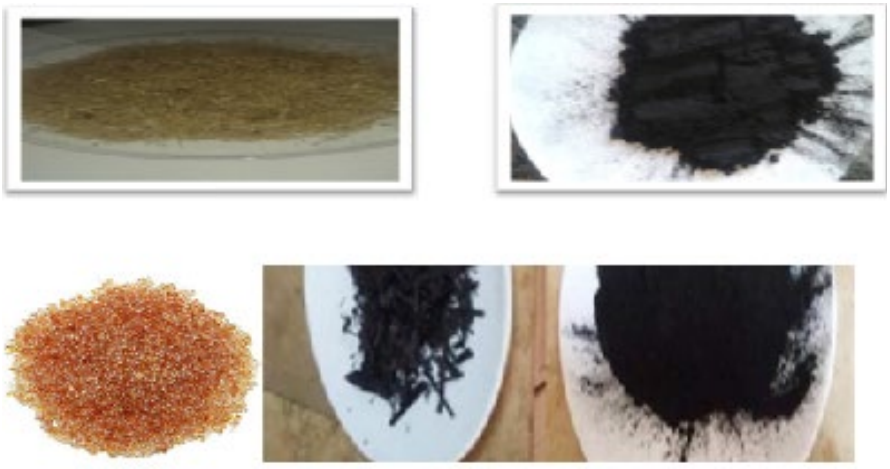

Figure 1. Images of activated carbon obtained from sugarcane bagasse before, after carbonization process, and natural zeolite.

2.2. Combination of Activated Carbon with Natural Zeolite

A series of natural zeolite (clinoptilolite) and activated carbon adsorbents were initially screened for the removal of Lead ions from its aqueous media. Based on typical material synthesis protocols for carbon-zeolite matrices, the preparation, optimization, and screening process to evaluate the final potassium hydroxide (KOH)- and phosphoric acid H_3PO_4-based composites follows a highly structured chemical activation, thermal conditioning, and mechanical sizing procedure. Adsorbent screening was performed in ratio according to Table 1.

Table 1. Natural zeolite and activated carbon adsorbents ratio for the removal of Lead(II) ions from aqueous media.

Sample No.	AC (KSCB) (H_3PO_4) + natural zeolite in (g)		AC (KSCB) (KOH) + natural zeolite in (g)	
	AC (KSCB) (H_3PO_4)	Zeolite	AC (KSCB) (KOH)	Zeolite
1	0.1	0.9	0.9	0.1
2	0.2	0.8	0.8	0.2
3	0.3	0.7	0.7	03
4	0.4	0.6	0.6	0.4
5	0.5	0.5	0.5	0.5
6	0.6	0.4	0.4	0.6
7	0.7	0.3	0.3	0.7
8	0.8	0.2	0.2	0.8
9	0.9	0.1	0.1	0.9

2.3. Evaluation of Activated Carbon

The samples of Kennan's Sugarcane Bagasse, (KSCB), Activated Carbon with KOH and H_3PO_4 modified with natural zeolite were evaluated five ways:

2.3.1. Energy Dispersive X-Ray Spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDX) analysis was carried out using (Perkin-Elmer 2400 Series) analyzer. The elemental compositions data of the two ACs, AC(KSCB) H_3PO_4 and AC(KSCB) KOH for carbon, hydrogen, nitrogen, sulfur and oxygen (CHNS-O) and other constituents, (Mg, Si, P, K, Ca, Al, and Fe), were determined.

2.3.2. Fourier Transform Infrared Spectroscopy

Transform Infrared (FTIR) spectroscopy (Shimadzu, Japan) was used to estimate the surface functional groups for the prepared AC(KSCB) H_3PO_4 and AC(KSCB) KOH samples and recorded within 400 - 4000 cm^{-1} range. The KBr pellet was used to record he sample's transmission spectra. Approximately 1.5% - 3.0% of each sample was mixed with dry grinded KBr. Then hydraulically pressed. The transparent in appearance and homogeneous pellets were dried at 100˚C for 24 hrs., and then inserted, for the analysis, into the IR sample holder [17].

2.3.3. Scanning Electron Microscopy (SEM)

AC(KSCB) H_3PO_4 and AC(KSCB) KOH samples were performed using the (JSM-6380LA) scanning electron microscope. The instrument was operated, at 55˚C inclination and 5 kV/SE, using accelerating voltage machine. Prior to analysis, samples were coated in a sputter shell unit, using Edwards Vacuum Components Ltd., Sussex, England, so as to reduce charging and improve the secondary electron signals for imaging. The micrographs were recorded via photographic techniques.

2.3.4. Process Parameters Effect

Batch experiments for adsorption of Pb(II) metal ions on AC(KSCB)KOH and AC(KSCB)H_3PO_4 each modified with natural zeolite, at 25˚C ± 0.5˚C., were conducted using Pb(II) metal ions aqueous solutions. A 1000 mg/L stock solution was prepared by dissolving appropriate weight of dissolving respective amount of its metallic nitric salt. To obtain different concentrations, the stock Pb (II) metal ions solution was diluted as required. For each run, a definite amount of AC(KSCB)KOH and AC(KSCB)H_3PO_4 each modified with natural zeolite was added to 25 ml Pb(II) solution taken in 100 ml Erlenmeyer flasks.

(1) pH Effect

An electronic pH—Meter (3510) was used to study the pH effect on metal adsorption, which was monitored over a pH range of 2 to 10. In this work, 25 ml separate solutions, 50 mg/L Pb(II) metal ion, was transferred into100 ml conical flasks, vigorously stirrer well for 60 mints. with 0.25 g AC(KSCB)KOH or AC(KSCB)H_3PO_4 each modified with natural zeolite, at 25˚C ± 0.5˚C. The filtered mixture was analyzed for residual metal ion concentration via Atomic Absorption Spectrophotometer (AAS). The equilibrium concentration (C_e) of Pb(II) and removal percentage were determined at the different pH.

(2) Contact Time Effect

To investigate contact time effect on Lead (II) metal ions removal percentage from its aqueous solutions, experiments were carried out using 75 mg/L initial concentration and 0.25 g AC(KSCB)KOH or AC(KSCB)H_3PO_4 each modified with natural zeolite dose at different contact times, 15 - 180 minutes. The filtered mixtures were well centrifuged. The filtrate of the metal ions residue was spectrophotometrically analyzed, using (AAS) [18]. The equilibrium concentration (C_e) of Pb(II) and removal percentage were determined at different contact time.

(3) Adsorbent Dosage Effect

Optimization of adsorbent dosage was carried out experimentally using different weights, 0.05 - 1.50 g, of AC(KSCB)KOH and AC(KSCB)H_3PO_4 each modified with natural zeolite. 75 ml of desired concentration of metal ion in 250 ml conical flask at the optimum pH for Pb(II) metal ion solutions. Aliquots concentration was analyzed to determine the extent of Pb(II) metal ions adsorption at equilibrium [19].

(4) Initial Concentration Effect

25 ml metal ions solutions with different initial concentrations between (10.0 - 150.0 mg/L) Pb(II) were contacted with optimized adsorbent dosage at the optimum pH. The mixtures were shaken well for the desired time at 25˚C ± 0.5˚C.

The mixtures were filtered, centrifuged and the concentrations of the metal ions adsorbed were determined [20].

2.3.5. Equilibrium Adsorption Studies

Lead(II) metal ions adsorption isotherms on AC(KSCB)KOH and AC(KSCB)H_3PO_4 each modified with natural zeolite, 25˚C ± 0.5˚C., were investigated by varying initial concentration (10.0 - 150.0 mg/L) Pb(II), at optimized pH, contact time, adsorbent dose, temperature, which were established after optimization of working parameters. To examine the equilibrium data obtained, Langmuir and Freundlich Isotherms models were used. The equilibrium metal ion adsorptive amounts (mg/g) in each batch modes were calculated using the following expressions [21]:

$$q_e = (V/w)/(C_O - C_e) \quad (1)$$

$$\%\text{Removal} = 100(C_O - C_e)/C_O \quad (2)$$

Where q_e is the amount of Pb(II) removed per unit weight of AC(KSCB)KOH or AC(KSCB)H_3PO_4 sample, each modified with natural zeolite in (mg/g), C_o and C_e are the initial and equilibrium concentrations of Pb(II) respectively in (mg/L), V is the treated volume of the solution in (L) and w is the mass dose of AC(KSCB)KOH or AC(KSCB)H_3PO_4 which modified with natural zeolite, in (g) [22].

3. Results and Discussion

3.1. Energy Dispersive X-Ray Spectroscopy (EDX)

The elemental composition of the adsorbents samples, AC(KSCB)KOH and AC(KSCB)H_3PO_4, were determined. Energy dispersive X-ray spectroscopy (EDX) data of the two ACs were presented. The ACs samples contain C, Ca, O, Fe, Mg, Al, and Si. The presence of the elements P and K, which are in corporate by chemical activation with, is due to H_3PO_4 and KOH activators respectively. The high adsorption efficiency of AC(KSCB)KOH and AC(KSCB)H_3PO_4 for Pb(II) metal ions solutions can also be confirmed by observing the EDX profiles results shown in Figures 2-3.

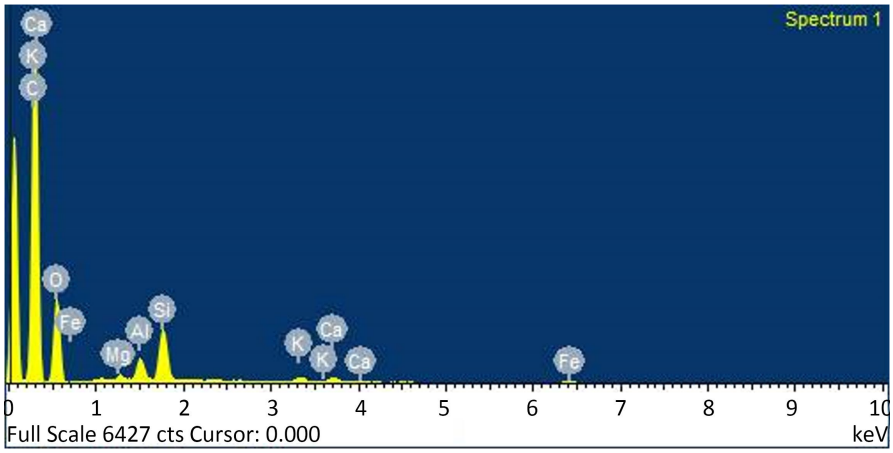

Figure 2. Sample No. (7) the best optimum one, when using KOH activator (0.85 g. KSCB + 0.15 g. natural zeolite).

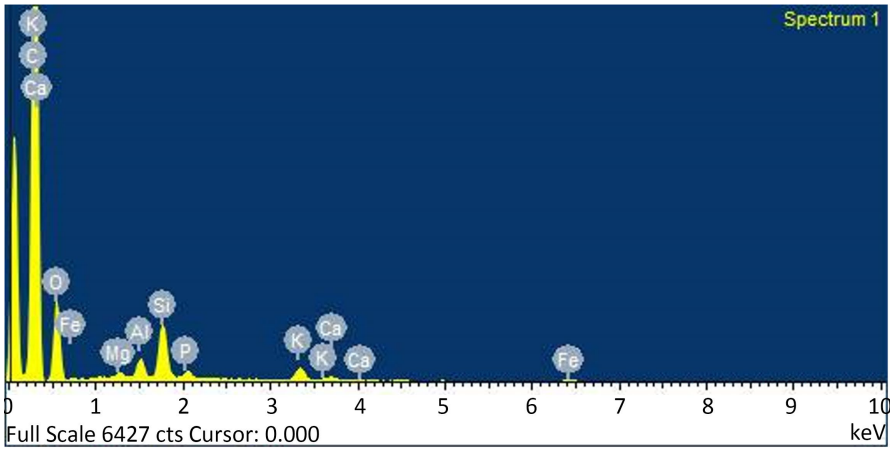

Figure 3. Sample No. (4) the best optimum one, when using H_3PO_4 activator (0.40 g. KSCB + 0.60 g. natural zeolite).

3.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FT-IR spectra of the two adsorbents, prepared activated carbon AC (KSCB)KOH and AC(KSCB)H_3PO_4 Combined with natural zeolite, were performed in order to explore their surface characteristics (**Figure 1**). The spectra display a number of absorption peaks, indicating the possible functional groups present on these bio sorbents, that may be responsible for the removal of Pb(II) metal ions from solution. The peak positions were observed at 3564.45, 1435.12, 1597.06, 1207.44, 1161.15 cm^{-1} for AC (KSCB)KOH and 3442.13, 1458.18, 1338.60, 1093.67, 1033.85, 802.39 and 1685.79 cm^{-1} for AC (KSCB)H_3PO_4. The bands at 3564.45 and 3442.13 cm^{-1} are due to N-H stretch (mainly primary and secondary amines) present on the adsorbents. The band observed at 1458.18, 1597.06 cm^{-1} are assigned to C=C bond (from alkenes), the bands at 1068.56 and 1161.15 cm^{-1} are assigned to C-O stretch (alcohols, ethers, acids, esters), 11701.62 and 1685.79 cm^{-1} corresponds to N-H bend of amines and amides, 1033.85 cm^{-1} is due to C-H bend of CH_2=CH_2 from vinyl groups. These peaks which correspond to different functional groups are possible sites for adsorption of Pb(II) metal ions by AC(KSCB)KOH or AC(KSCB)H_3PO_4 adsorbents. The peak intensities indicate that especially the OH groups, carboxylic acids or esters, the C-O stretch of either alcohols ethers, the N-H stretch of the primary or secondary amines, N-H bend of the amine or amides and the C=C stretch of the alkenes may play a major role in the adsorption of Pb(II) ions from the aqueous solutions. These functional groups contain either—electron which is electron—rich or lone pairs on nitrogen or oxygen, with which they can coordinate with the metal ions leading to their adsorption. Comparing **Figures 4-5**, one can conclude that, some of these peaks are either absent or new ones detected. This may be due to surface variation resulting from the combination of the AC (KSCB)H_3PO_4 with natural zeolite.

3.3. Scanning Electron Microscopy (SEM)

Scanning electron microscopy images of the modified activated carbons with

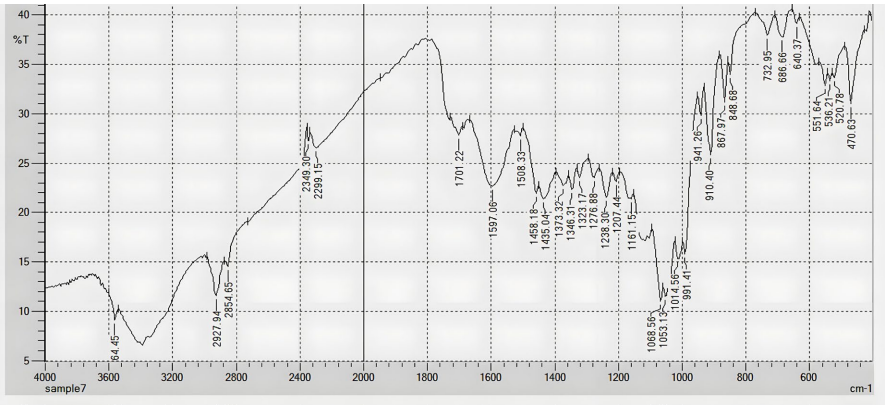

Figure 4. FTIR spectrum of AC (KSCB)KOH combined with natural zeolite.

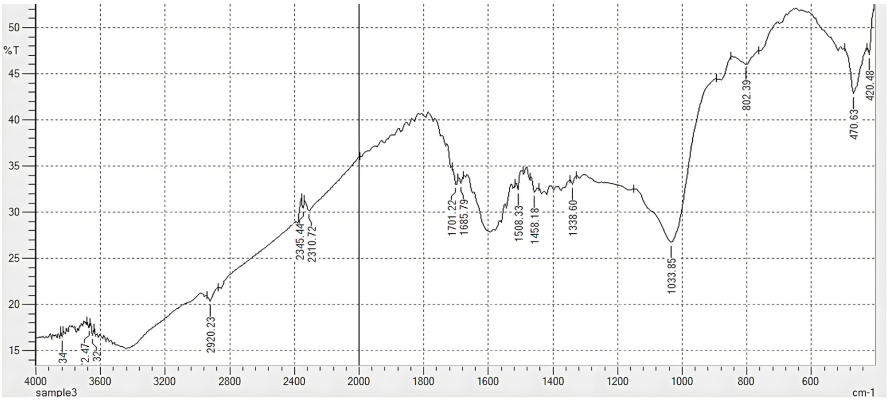

Figure 5. FTIR spectrum of AC (KSCB)H_3PO_4 combined with natural zeolite.

natural zeolite when using KOH and H_3PO_4 as activators are shown in **Figures 6-7**. The SEM scans show that the optimum prepared samples of the modified activated carbons {Samples No. 7, the best optimum one when using KOH activator (0.85 g KSCB + 0.15 g Zeolite)} and {Sample No. 4, the best optimum one when using H_3PO_4 activator (0.40 g KSCB + 0.60 g Zeolite)} has a more developed porous structure than the other prepared ones when using other different fractions from KSCB/KOH modified with zeolite and KSCB/H_3PO_4 modified with zeolite. The scans further show that, the treatment enhanced the porous structure of the modified activated carbon leading to the development of channels, pores and great increase in the surface area. The enhancement in surface area, in the case of the treated modified samples, is likely due to the interaction of zeolite and ashes, and also due to the basic and acidic nature of the KOH and H_3PO_4 activators respectively. Nevertheless, the scans showed that, zeolite has deposited on the surface of the treated activated carbon samples. On the other hand, the increase in the surface area of the treated KSCB activated carbons is likely due to the opening of the structure of the biomass due to the acidic and basic digestion in the KOH and H_3PO_4 solution. The deposition of the zeolite is observed to be more thoroughly distributed through the ridges, channels and pores of the treated KSCB activated carbons.

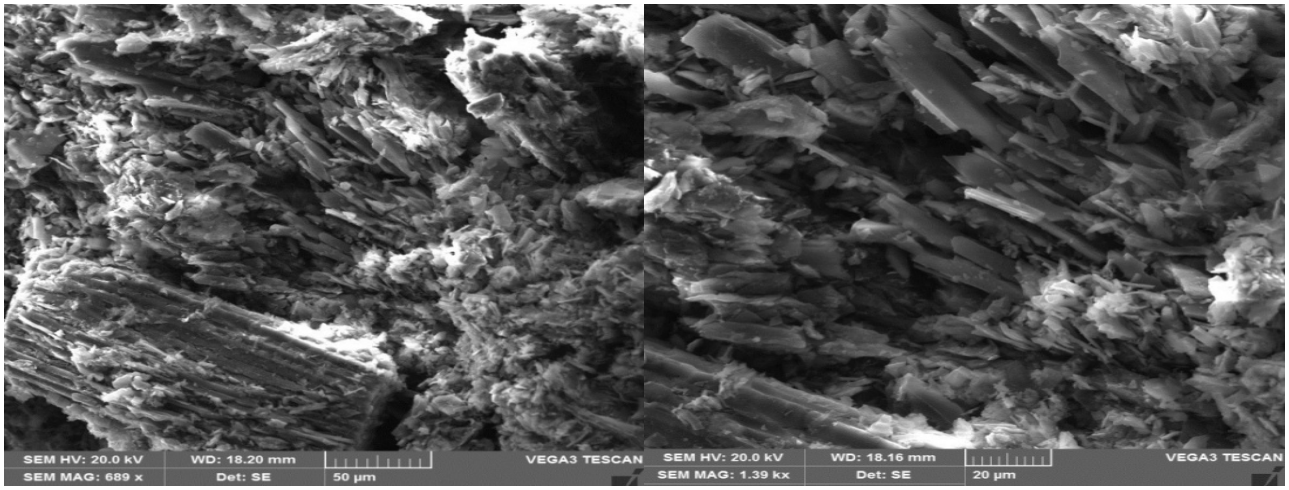

Figure 6. Sample No. (7) the best optimum one when, using KOH activator (0.85 g. KSCB + 0.15 g. natural zeolite).

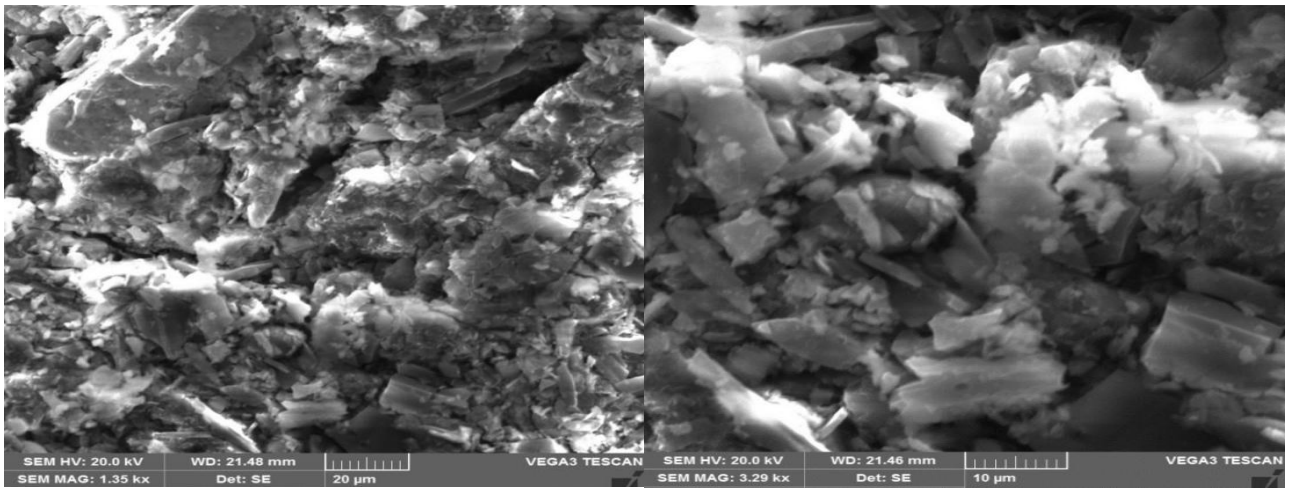

Figure 7. Sample No. 4 the best optimum one when using H_3PO_4 activator (0.40 g. KSCB + 0.60 g. natural zeolite).

3.4. Process Parameters Effect

3.4.1. pH Effect

The adsorption of Pb(II) metal ion from its aqueous solutions on adsorbent is significantly influences by solution pH, which has been introduced as one of the effective factors in process parameters [9]. Kennan's sugarcane bagasse AC (KSCB)KOH/H_3PO_4 prepared by chemical activators (KOH and H_3PO_4). Combined with natural zeolite were engaged for Pb(II) removal at different pH values (2 - 10). The preliminary experiments at definite experimental conditions (initial Pb(II) concentration 75.0 mg/L, adsorbent dose 0.25 g/100 ml, contact time 60 min, and temperature 25˚C ± 0.50˚C) were performed. The removal of the metal ions was affected by changes in pH as shown in **Figure 8**. It is proved from the figure that adsorption percentage was higher at pH(5 and 6). On the other hand, the highest average removals of Pb(II) observed at pH(5 and 6), was 96.83% and 87.58% when using H_3PO_4 and KOH activators respectively. Generally, metal ions are more soluble at lower pH values and this enhances their adsorption. Removal

of metal ions at higher pH values could be attributed to their hydroxides formed, which results in precipitates, this is consistent with the observation. The results obtained are in close agreement with previously reported investigations [9] [10].

3.4.2. Adsorbent Dose Effect

The adsorbent dose, of AC(KSCB)KOH or AC(KSCB)H_3PO_4 modified with natural zeolite, as effective factor on removal percentage of Pb(II) was studied. The results were illustrated in Figure 9. Different series of adsorbent doses, (50 - 1500 mg)

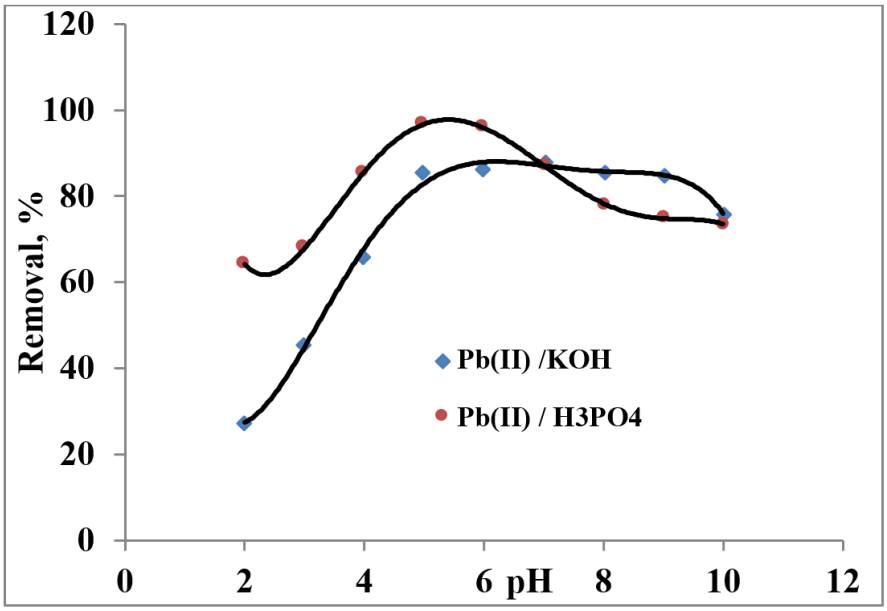

Figure 8. Effect of pH on Pb(II) removal by AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite (C_O = 75 mg/L, dose = 0.25 g/ml, contact time = 60 min., T = 25˚C ± 0.50˚C).

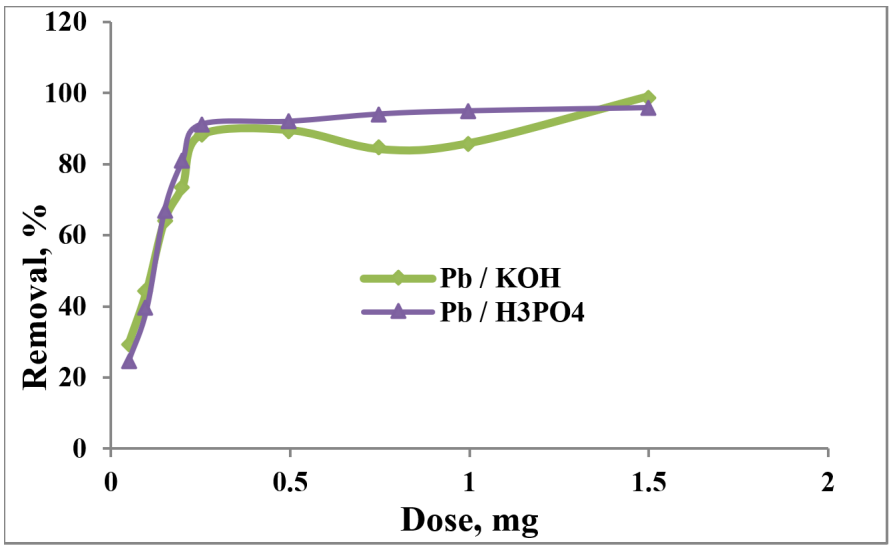

Figure 9. Effect of adsorbent dose on Pb(II) removal by AC (KSCB) Activated Carbon with KOH/H_3PO_4 combined with zeolite (C_O = 75 mg/L, pH = {5&6}, contact time = 60 min., T = 25˚C ± 0.50˚C).

were considered and other process parameters were maintained constant, pH (5&6), using a concentration of 75 mg/L, contact time - 60 min, at 25˚C ± 0.50˚C. A significant increase in removal efficiency with increasing adsorbent dose up to a maximum of 0.25 g/ml was found. The results showed that the corresponding optimal removal percentage were 91.26% at (pH = 6) and 88.24 % at (pH = 5) when using H_3PO_4 and KOH activators respectively. In contract, the obtained results showed that any further addition over the above mentioned weight, (>0.25 g), will not make any enhancement in the efficiency of adsorption, where exactly negligible increase of removal efficiency over the identifiable specific adsorbent amount. The initial increase in removal of Pb(II) ions from their aqueous solutions with increasing adsorbent mass suggesting that it can be explained by the increase in the number of exchangeable sites on AC(KSCB)KOH or AC(KSCB)H_3PO_4 modified with natural zeolite for Pb(II) metal ion removal, after which equilibrations was attained [10].

3.4.3. Contact Time Effect

The effect of contact time on the removal of Pb(II) using AC (KSCB) KOH and H_3PO_4 combined with zeolite were shown in **Figure 10**. The adsorption capacity of metal ions increased by a nearly even dynamic trend with increasing time, reached equilibrium after approximately 60 mints; the adsorption capacity sequence was consistent with the result obtained in initial concentration tests. A constant adsorption is indicative of equilibration due to saturation of adsorption sites. Rapid removal of Pb(II) ions during the initial stages was due to the large initial concentration gradient between its concentration in solution and the number of available unoccupied sites on surface of AC(KSCB)KOH or AC(KSCB)H_3PO_4 modified with natural zeolite. The removal of Pb(II) was 90.60% at (pH = 5), and 86.13% at (pH = 6) each at 60 mints. as contact time, when using KOH and H_3PO_4 activators respectively.

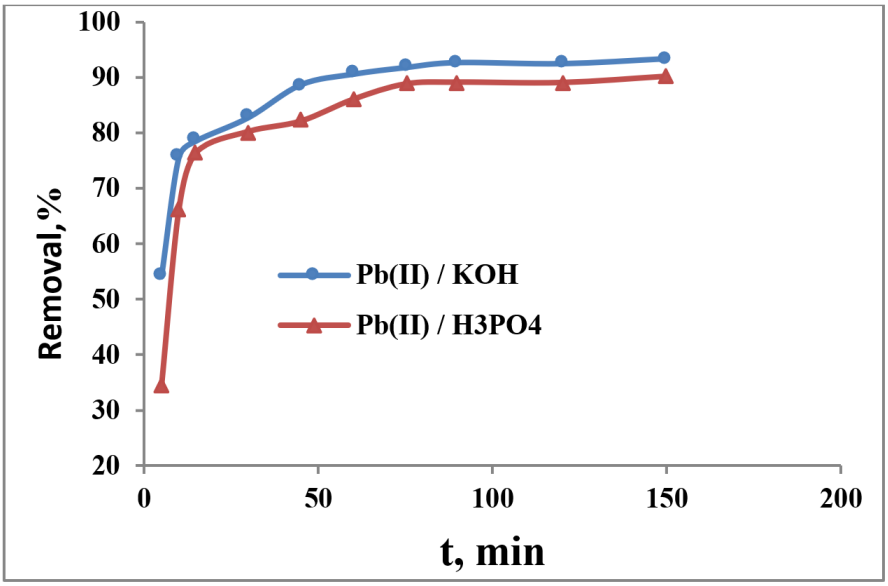

Figure 10. Effect of contact time on PbII) removal by AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite, (C_O = 75 mg/L, pH = {5&6}, dose = 0.25 g/ml, T = 25˚C ± 0.50˚C).

3.4.4. Initial Concentration Effect

The initial concentration of Pb(II) is an essential effective parameter since it changes over abroad extent in effluents applications. Different initial concentrations were used to carry out batch adsorption experiments. The variation of removal percentage for these different initial concentrations, using AC(KSCB) activated carbon with KOH or H_3PO_4 each combined with natural zeolite were shown in Figure 11. The figure shows an excellent performance for Pb(II) metal ions initial concentrations, at equilibrium state and the most favorable initial concentration, (75.0 mg/L) under the experimental conditions. It is also clearly as well as observed, that the removal percentage of Pb(II) when using KOH and H_3PO_4 as activators were sufficiently high, (76.01%, 68.16%) respectively and no significant additional increase as the concentration increases.

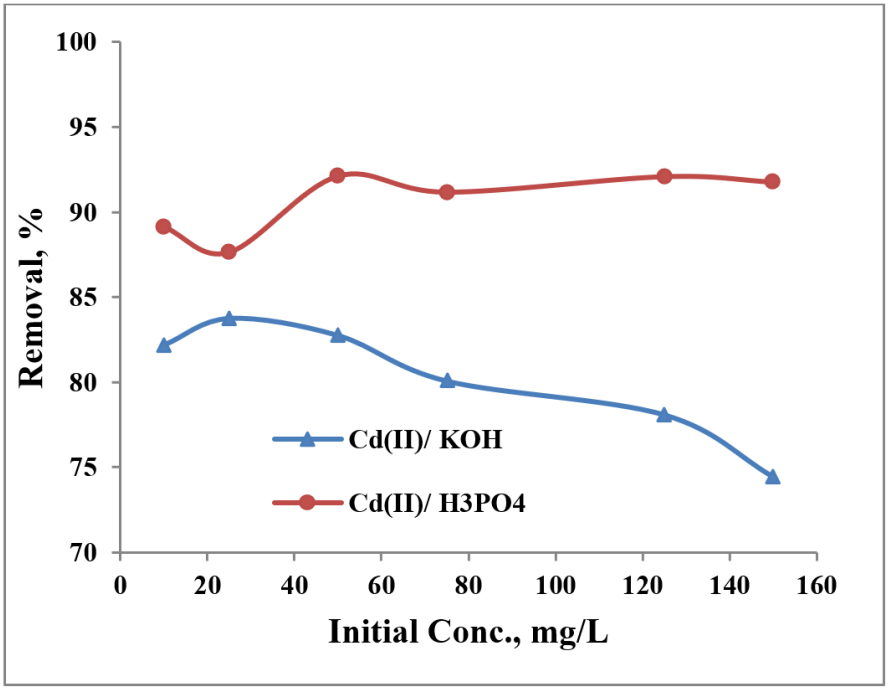

Figure 11. Effect of initial concentration on Pb(II) removal by AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite, pH = {5&6}, dose = 0.25 g/ml, contact Time = 60 min. , T = 25˚C± 0.50˚C.

3.5. Adsorption Isotherm

The adsorption capacity of any adsorbent is conceder an effective specific function of concentration. The shape of an isotherm provides information about the adsorption affinity of molecules and stability of the interactions between adsorbent and adsorbate [23]. The equilibrium adsorption isotherms were described by plotting solute concentration in the solid phase (q_e) against liquid phase concentration (C_e). Langmuir and Freundlich adsorption isotherms were applied to the experimental data to investigate the adsorption behavior of Pb(II) metal ions on prepared AC (KSCB) Activated Carbon with KOH and H_3PO_4 each modified with natural zeolite, at different conditions of process parameters.

3.5.1. Langmuir Isotherm

The Langmuir isotherm is applicable to homogeneous sorption where the sorption of each sorbet molecule on to the surface has equal sorption activation energy and is represented as follows [24].

$$C_e/q_e = 1/q_m K_L + C_e/q_m \quad (3)$$

Where q_m (mg/g) is the maximum adsorption capacity of the adsorbent, K_L (L/mg) is the affinity parameter or Langmuir isotherm constants related to adsorption capacity (mg g^{-1}), which can be correlated with the variation of the suitable area and porosity of the adsorbent which implies that large surface area and pore volume will result in higher adsorption capacity.

Dividing Equation (3) by C_e one can obtain:

$$1/q_e = 1/q_m + 1/q_m K_L C_e \quad (4)$$

The analyzed adsorption data, according to Langmuir isotherm linear form (Equation (4)), was described by plotting of $1/q_e$ versus $1/C_e$. The obtained linear plots shows that, the adsorption obeys to the Langmuir isotherm model, **Figure 12**. The constant values were calculated from the slope ($1/q_m K_L$) and intercept ($1/q_m$) and reported in **Table 2**. According to R^2 values, (0.9900 and 0.9890) for Pb(II) removal when using KOH and H_3PO_4 activators respectively, the Langmuir equation well fitted the experimental adsorption data for Pb(II) removal using AC(KSCB) Activated Carbon with KOH/H_3PO_4 combined with natural zeolite, thereby representing a monolayer adsorption in each case.

Table 2. Langmuir Freundlich isotherm constants of AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite for Pb(II) removal at 25˚C± 0.50˚C. with their correlation coefficients.

Metal ion	Langmuir					Freundlich		
	Activaitor used combined with natural zeolite	q_m (mg/g)	K_L (L/mg)	R_L	R	K_f (mg/g)	n	R
Pb(II)	KOH	588.24	138.77	0.0053	0.9951	5.85	1.27	0.9786
	H_3PO_4	161.29	92.39	0.0070	0.9947	1.87	0.94	0.9894

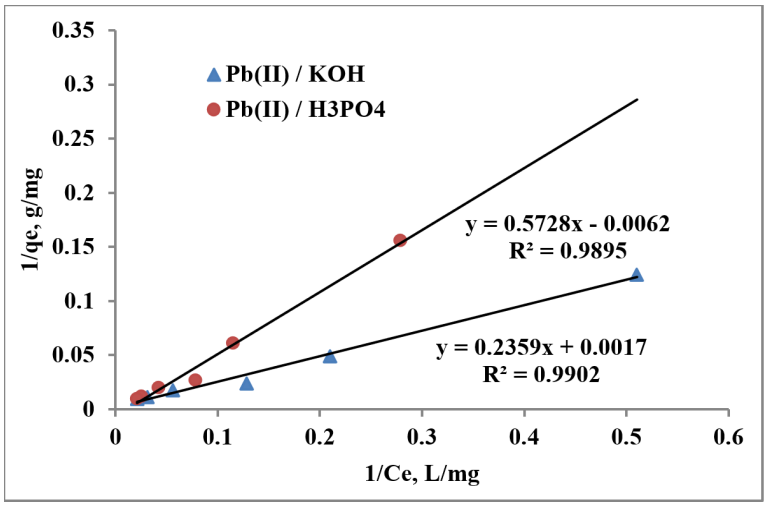

Figure12. Langmuir isotherms of AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite for Pb(II) removal 25˚C ± 0.50˚C.

To investigate in details the Langmuir isotherm, a dimensionless parameter, Namely, separation factor R_L, [25], defined by Equation (5):

$$R_L = 1/(1 + K_L C_O) \tag{5}$$

Where C_O is the initial metal ion concentration. The R_L values for the prepared adsorbent, AC (KSCB) with KOH and H_3PO_4 combined with natural zeolite, were between 0.0053 and 0.0073 which were in the range of: $0 < R_L < 1$; hence the prepared adsorbent sample show satisfactory adsorption of Pb(II) metal ions under the specified conditions [24] [25]. In addition, R_L was closed to zero at high C_O values, thereby suggesting that the prepared adsorbent sample undergo irreversible metal ion adsorption process at high initial metal ion concentration.

The maximum adsorption capacity of the prepared adsorbent samples were compared with those of various conventional adsorbent are tabulated in **Table 3**. Although the adsorption conditions differed among them, the prepared adsorbent sample had a level of adsorption capacity similar to that of conventional adsorbents, thereby suggesting that the prepared adsorbent samples can be used for the removal of Pb(II) metal ions. The reasonably high regression coefficients which confirm a well-fitting to the Langmuir equation are summarized in **Table 2**.

Table 3. Comparison of heavy metal removal capacities(mg/g) by different adsorbents.

Adsorbent	Pb(II)	Sources
African white star apple shell	8.40	[26]
Sphagnum moss peat	12.30	[27]
Maple sawdust	3.19	[28]
AC (KSCB)KOH combined with natural zeolite	588.24	This Study
AC (KSCB)H_3PO_4 combined with natural zeolite	161.29	

3.5.2. Freundlich Isotherm

Freundlich empirical model can be applied to non-ideal sorption on heterogeneous surfaces as well as multilayer sorption and is expresses by the following equation [24].

$$q_e = K_F C_e^{1/n} \tag{6}$$

Where n and K_F are investigative constants of the intensity of the sorption and the relative sorption capacity of the sorbent. Equation (6) can be linearized in the form of Equation (7) and the constants can be determined [24]:

$$\ln q_e = \ln K_F + 1/n \ln C_e \tag{7}$$

Where q_e is the extent of Pb(II) adsorbed per unit mass of AC(KSCB)KOH or AC(KSCB)H_3PO_4 modified with natural zeolite in (mg/g) and C_e is the equilibrium concentration of Pb(II) in (mg/L). **Figure 13** show the fit of data to Freundlich isotherm indicates the surface heterogeneity of AC(KSCB)KOH and AC(KSCB)H_3PO_4 each modified with natural zeolite. $1/n$ is the heterogeneity factor and it is a feature measure of the deviation from linearity of Pb(II) adsorption. The n value indicates the degree of non-linearity between solution concentration

and adsorption as follows: if the value of $n = 1$, the adsorption is linear; $n < 1$, the adsorption process is chemical; if $n > 1$, the adsorption is a favorable physical process. The correlation coefficients, $R = 0.9570$ and 0.9790, obtained from the Freundlich model when using KOH and H_3PO_4 as activators respectively, were comparable to that obtained from Langmuir model (Table 2). This result indicates that the experimental data fit to the Freundlich model, and $n > 1$ when KOH activator was used. The values of Freundlich constants with the correlation coefficients are presented in Table 2.

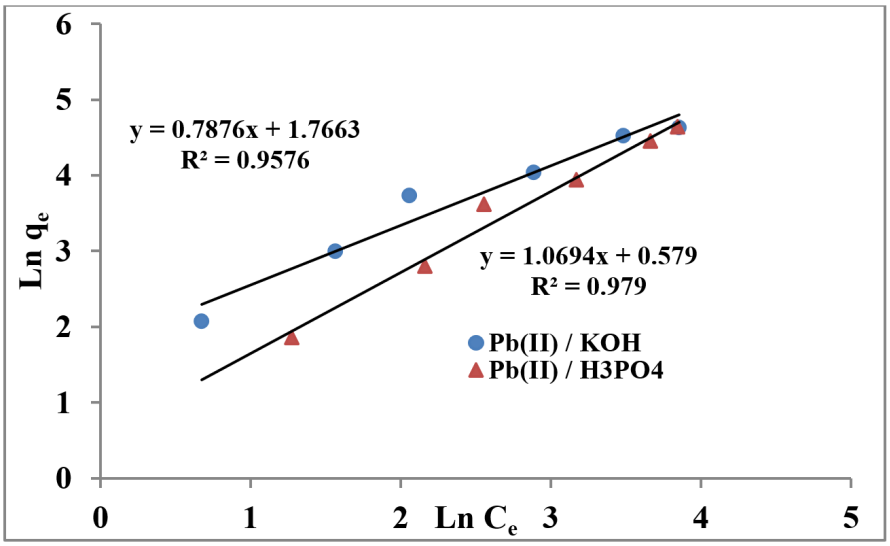

Figure 13. Freundlich isotherms of AC (KSCB) activated carbon with KOH/H_3PO_4 combined with zeolite for Pb(II) removal at 25˚C ± 0.50˚C.

As a result from these isotherms one can show that, the equilibrium adsorption amount of AC(KSCB) Activated Carbon with KOH and H_3PO_4 combined with natural zeolite for Pb (II) removal with different initial concentrations, and according to the fitting curves and correlation coefficients(R^2), Langmuir model was more suitable to describe the adsorption of Pb(II) onto the prepared adsorbent sample, indicating that the surface of AC(KSCB) Activated Carbon with KOH and H_3PO_4 combined with natural zeolite were homogeneous and the adsorption was monolayer, where it adsorption capacity (q_m) for Pb(II) was 588.24 mg/g when using KOH activator, while it was 161.29 mg/g when using H_3PO_4, the obtained results are tabulated in Table 3.

4. Conclusion

The findings in this study revealed that Modified Kennan's sugarcane baggase activated carbon with natural zeolite can be effectively be employed as an eco-friendly adsorbent for the removal of Pb(II) ions form aqueous solutions. It will also provide an ideal technology to utilize and convert this adsorbent into valuable product which can be commercialized for the removal of contaminants from aqueous phase. The data from the batch adsorption studies provided essential in-

formation in terms of optimum pH, contact time, adsorbent dose and Lead(II) initial concentration.

Conflicts of Interest

The authors declare no conflicts of interest.

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