

# Adsorption Study of Pb(II) Ions on the Blast Furnace Slag (BFS) from Aqueous Solution

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**Abstract:** In this work, blast furnace slag (BFS) was used as an adsorbent material for the removal of Pb (II) ions in solution in batch mode. The physico-chemical analysis used indicated that the BFS is essentially composed of silica, lime, and alumina. Its specific surface area was  $275.8 \text{ m}^2/\text{g}$  and its PZC was around 3.8. The adsorption study indicated that the maximum amount of Pb (II) adsorbed under optimum conditions (agitation speed ( $V_{ag}$ ): 150 rpm; pH: 5.4; particle size ( $\phi_s$ ):  $300 \mu\text{m}$ , T:  $20^\circ\text{C}$ ) was  $34.26 \text{ mg/g}$  after 50 minutes of agitation, and adsorption yield was best for feeble initial concentrations. The most appropriate isothermal model was that of Langmuir, and the adsorption speed was better characterized by the pseudo-second order kinetic model. The adsorption mechanism study revealed that internal diffusion is not the only mechanism that controls the adsorption process and there is also an external diffusion, which contributes enormously in the transfer of Pb (II) from solution to adsorbent. Thermodynamic study indicated that the Pb (II) adsorption on the blast furnace slag (BFS) was spontaneous, exothermic, and that the adsorbed Pb (II) is more ordered at the surface of the adsorbent.

**Keywords:** Adsorption, Slag, Pb (II), Kinetics, depollution.

## 1. INTRODUCTION

Liquid discharge containing Pb (II) is harmful to humans and their environment due to its harmful effects [1]. In fact, the ions Pb (II) are hardly degradable and have a negative impact on the environment's self-cleaning processes and their bioaccumulations, favoring the toxicity of living organisms [2]. Pb (II) can come from several production activities such as Mining, production of non-ferrous metals, foundry waste, alloys, paints, storage batteries, cable sheaths, products for use in plastics and industries automobiles [3]. Removal of such a harmful element requires treatment of choice, such as chemical precipitation [4], coagulation/flotation [5], membrane technologies [6], ion exchange [7], electrochemical technologies [8] and adsorption phenomenon [9]. Amongst these processes, adsorption is considered to be one of the best processes employed for the removal of metal ions in solution due to its simplicity, high efficiency, and reasonable price [10]. According to the literature, adsorbents used in the Pb (II) removal processes in solution are generally the carbon-based adsorbents [11], clay minerals [12], polymers [13], wood waste [14], nanocomposite [15] and nanomaterials [16]. In this study, blast furnace slag (BFS) has been chosen as a

trustworthy, present in large quantities, and less expensive adsorbent. This material is a co-product of the metallurgical steel industry. It is formed during the production of pig iron from iron ores in the blast furnace. In the world, the annual production of BFS is very important. It amounts to tens of millions of tons [17], which represents a real environmental problem and a waste of considerable financial resources [18]. Previous researches have indicated that blast furnace slag is an effective adsorbent in the field of water treatment, especially in the elimination of metal ions, phosphorus, and dyes. Indeed, El-Dars et al. [19] mentioned that water-cooled blast furnace slag showed good potential as an adsorbent to remove divalent nickel ions from aqueous solutions. Scott et al. [20] reported that steel slags have been shown to be an effective means of phosphorus removal and a potential aid in reducing point and non-point source phosphorus pollution in fresh waters. However, Dhmees et al. [21] demonstrated that silica nanoparticles obtained from blast furnace slag and desilicated blast furnace slag can be used as a low-cost adsorbent to remove methylene blue from water.

The principal objective of this study was to introduce blast furnace slag (BFS) in the field of pollution control of waters containing Pb (II). The

approach consisted of evaluating the adsorption capacity of BFS to eliminate Pb (II) in solution under different experimental conditions as a first step. The second step is to define the adsorption isotherms, calculate the reaction velocity, identify the mode of Pb (II) diffusion from the solution to the BFS, and investigate the nature of the elimination process. It is obvious that the preparation and characterization of the solid had to be done beforehand. In this work, X-ray diffraction, X-ray fluorescence, and infrared were used for the physico-chemical characterization of BFS. However, its specific surface area (SSA) was measured using the BET method. Otherwise, the agitation speed ( $V_{ag}$ ), pH, temperature, particle size ( $\phi_s$ ) and initial concentration were used to assess the yield of the Pb (II) adsorption on BFS. Langmuir, Freundlich and Temkin models were used for presenting the adsorption isotherms. Kinetic models were utilized to describe the kinetics and mechanisms of the adsorption process. The thermodynamic parameters were investigated to study the energy exchanges. The purpose of this study is to confirm that BFS is a reliable adsorbent that can contribute to the decontamination of water containing metal ions.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Treatment of BFS

The Samples of the BFS were collected at the El-Hadjar steel complex Annaba/Algeria, in the form of rocks with dark color. The washing performed at the crude slag is represented as follows [22]:

- The considered BFS samples were washed with distilled water and air dried for 48 hours.
- The washed samples were grinded and sieved to various size: 200, 300, 400 and 500  $\mu\text{m}$ .
- Samples with different grain sizes were separated, washed with distilled water, steamed at 105°C and stored in plastic boxes for subsequent use in adsorption processes.

### 2.2. Analytic Methods

Pb (II) concentration was measured by atomic absorption spectroscopy method using PerkinElmer 3110 equipments. The pH of solution was measured with an Ericsson pH meter. The characterization was carried out by X-ray fluorescence (Siemens SRS 3000), X-ray diffraction (Rigaku Ultim IV) and Fourier

transform infrared spectrometer (Perkin Elmer).

### 2.3. Adsorption Protocol

A series of batch experiments were conducted to evaluate the Pb (II) adsorption process on BFS. These experiments will allow us to determine the maximum adsorbed capacity, investigate the adsorbate-adsorbent interaction, define the reaction speed order of the process, determine the method of Pb (II) diffusion from the solution to the BFS surface, and specify the nature of adsorption. Adsorption kinetics were investigated by adding one gram of BFS to aqueous solutions prepared with Pb (II) nitrate ( $\text{Pb}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) at a low level. The concentrations prepared vary from 10 to 80 mg/L and the solution volume is 1 liter. The continuous mixing of the solution was ensured during all the tests by mechanical stirrer at different speeds. The temperature was controlled with a water bath equipped with a thermostat. The adsorption kinetics were followed by sampling of 5 ml every 10min. The samples taken were stocked in flasks and the concentration of Pb (II) ions was measured using atomic absorption spectrometry (AAS).

The results of Pb (II) adsorption in this study were analyzed in terms of adsorptive capacity ( $q$ ), as determined by equation 1:

$$q_t = \frac{C_0 - C_t}{m} \times V \quad (1)$$

Efficiency of Pb (II) adsorption in this study is calculated by the following equation (eq. 2):

$$\%R = \frac{C_0 - C_e}{C_0} \times V \quad (2)$$

Where:  $C_0$ : Initial concentration of the metal solution (mg/L);  $C_t$ : Concentration of the metal solution after a time  $t$  (mg/L);  $C_e$ : Concentration of the metal solution after at equilibrium (mg/L);  $V$ : Volume of the solution (L);  $m$ : Adsorbent mass (g).

The operating conditions undertaken in this study are given as follows:

- Equilibrium time:  $C_0$ : 30 mg/L;  $V_{ag}$ : 150 rpm; pH: 4.4;  $T = 20^\circ\text{C}$ ;  $\phi_s$ : 400  $\mu\text{m}$ ;  $M_s$ : 1 g.
- Effect of  $\phi_s$ :  $C_0$ : 30 mg/L;  $V_{ag}$ : 150 rpm; pH: 4.4;  $T = 20^\circ\text{C}$ ;  $\phi_s$ : 400  $\mu\text{m}$ ;  $M_s$ : 0.2, 0.4, 0.6, 0.8, 1, 1.2, 1.4 g.
- Effect of pH:  $C_0$ : 30 mg/L;  $V_{ag}$ : 150 rpm; pH=2, 4.4, 5.4 and 6;  $T$ :  $20^\circ\text{C}$ ;  $\phi_s$ : 400  $\mu\text{m}$ ;  $M_s$ : 1 g.
- Effect of  $T$ :  $C_0$ : 30 mg/L;  $V_{ag}$ : 150 rpm; pH: 5.4;  $T$ : 20, 40 and  $50^\circ\text{C}$ ;  $\phi_s$ : 400  $\mu\text{m}$ ;  $M_s$ : 1 g.
- Effect of  $\phi_s$ :  $C_0$ : 30 mg/L;  $V_{ag}$ : 150 rpm; pH:

5.4; T: 20°C; Øs: 200, 300 and 400 µm. Ms: 1 g.

- Effect of C<sub>0</sub>: C<sub>0</sub>: 10-80 mg/L; V<sub>ag</sub>: 150 rpm; pH: 5.4; Øs: 300 µm, T: 20°C; Ms: 1 g.

Where: BFS: the blast furnace slag C<sub>0</sub>: initial concentration (mg/L); V<sub>ag</sub>: agitation speed (rpm); Øs: BFS particle size (µm); Ms: BFS mass (g); T: solution temperature (°C).

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of BFS

The BFS from Sider El-Hadjar complex is mainly composed of alkaline oxides CaO, MgO and acidic oxides Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>. In which the content of CaO is 37.2%, MgO is 3.12%, Al<sub>2</sub>O<sub>3</sub> is 8.2%, and SiO<sub>2</sub> is 41.1% (table 1). In addition, BFS has a small amount of other metal oxides (Fe<sub>2</sub>O<sub>3</sub>, NiO, K<sub>2</sub>O, and Na<sub>2</sub>O) (table 1).

**Table 1.** Table1. Chemical composition of BFS [22].

| Element                        | Mass % |
|--------------------------------|--------|
| CaO                            | 37.2   |
| Al <sub>2</sub> O <sub>3</sub> | 8.2    |
| SiO <sub>2</sub>               | 41.1   |
| Fe <sub>2</sub> O <sub>3</sub> | 2.51   |
| MgO                            | 3.12   |
| MnO                            | 2.64   |
| K <sub>2</sub> O               | 0.3    |
| Na <sub>2</sub> O              | 0.7    |
| LOI                            | 4.23   |

The tests realized by X-ray diffraction indicated that the BFS is essentially composed of the lime,

the silica and the alumina in less quantity (Fig. 1(a)). FT-IR spectrum of fraction shows the stretching vibrations of 1793, 879 and 715 cm<sup>-1</sup> whose origins are due to the stretching vibration of COCa<sub>3</sub> (Fig. 1(b)). The observed peak at 1437cm<sup>-1</sup> indicated the bond elongation CO. However, the Si-O-Si and Al-O bonds were indicated by the vibrations bands respectively at 1007 cm<sup>-1</sup>, 634cm<sup>-1</sup> (Fig. 1(b)). These observations were justified by the results obtained by X-ray fluorescence.

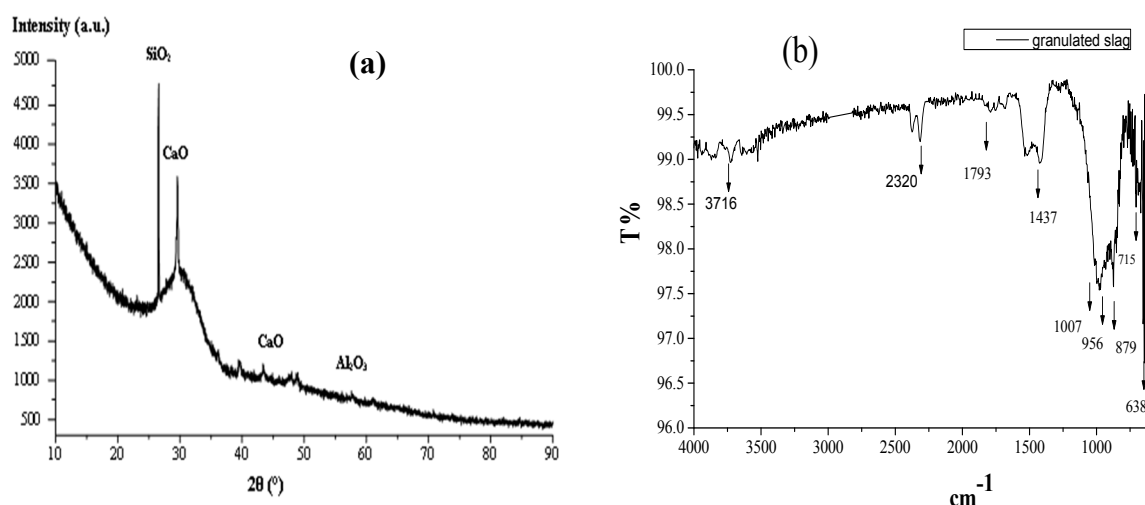
The specific surface areas (SSA) of the BFS particles were obtained by using the nitrogen gas adsorption-desorption method. The Brunauer, Emmett, and Teller (BET) model was used to analyze the isotherm data for nitrogen gas desorption at 77 K. The result of the investigations has shown that the specific surface is 275.8 m<sup>2</sup>.g<sup>-1</sup>.

#### 3.2. Adsorption Studies

##### 3.2.1. Effect of agitation time

The contact time required to effectively remove pollutants by the adsorption process is a very considerable variable because it tells us about the equilibrium time and the saturation of the adsorbent.

The kinetic study revealed that Pb (II) adsorption was rapid for the first 30 minutes, then gradually decreased until it was non-existent. Increasing the contact time further yielded no further adsorption for 190 min, which followed (Fig. 2(a)). This means that the adsorbent has reached the saturation phase.



**Fig. 1.** a) Diffractogram of BFS sample [22], b) infrared spectrum of BFS sample.



Fig. 2. a) Effect of agitation time, b) Effect of pH, c) Zeta potential as a function of pH.

Indeed, the stopping of the adsorption process is generally generated by the saturation of the surface of the adsorbent, that is to say, the total occupation of the active sites of adsorption by the lead ions. Consequently, we consider 50 min as the equilibrium time of Pb (II) adsorption by BFS.

### 3.2.2. Effect of initial pH

The pH of the solution is an important parameter in the adsorption phenomenon because it affects the form of metal in solution, as well as the surface properties of the adsorbent [23]. In this work, The effect of pH on Pb (II) adsorption was investigated over a pH range from 3 to 6.2 (3, 4.4, 5.4, and 6.2), at a contact time of 50min (Fig. 2(b)).

At pH 3, the adsorption process was the least efficient (Fig. 2(b)). For this medium, the strong presence of  $H^+$  ions slows down the transfer of Pb (II) ions from the solution to the adsorbent [24].

As initial pH increased from 3 to 5.4, the residual concentration decreased from 17.88 to 5.52 mg/L (Fig. 2(b)). Indeed, the efficiency of adsorption can be explained by the effect that the pH of the solution has favourably influenced the surface charges of adsorbent by turning it negative [25]. Due to this result, we hypothesized that Pb (II) adsorption on blast furnace slag was caused by the electrostatic interaction [22]. Indeed, Fig. 3(a) shows that the pzc of the adsorbent corresponds to  $pH = 3.8$ , which indicates that the surface of the blast furnace slag is negatively charged at a pH greater than 3.8.

For an initial pH of 6.2, the quantity eliminated is more important. The concentration at equilibrium and the rate of elimination are, respectively: 2.15 mg/L and 92.83%. This outcome was obtained by the phenomena of adsorption and chemical precipitation. Indeed, the lead ions ( $Pb^{++}$ ) are

precipitated by the hydroxide anion that forms the precipitate of lead hydroxide when the pH approaches 7 [26]. Accordingly, pH= 5.4 value was selected as optimum pH for Pb (II) adsorption. A similar study found that steel slag eliminates the most Pb (II) at pH 5 [27].

### 3.2.3. Effect of temperature

The solution temperature has important effects on the adsorption process [28]. In this context, the effect of temperature on Pb (II) adsorption was investigated. The temperatures studied are varied from 20 to 50°C (Fig. 3(a)).

The results showed that the Pb (II) adsorption capacity decreased with the increase in temperature (Fig. 3(a)). With increasing temperature, the mobility of Pb (II) ions increased, thereby resulting in the escape of ions from the solid phase to the liquid phase. Therefore, the lead adsorption process on the BFS is becoming less and less favorable [29]. This result led us to predict that the Pb (II) adsorption process on BFS in solution is exothermic [30].

### 3.2.4. Influence of particles size

The adsorbent granulometry has a predominant role in the rate of transfer of metal ions from the solution to the adsorbent [31]. In this context, we have optimized the particle size of BFS using diameters varying from 200 to 500  $\mu\text{m}$  (Fig. 3(b)). According to the test results, Pb (II) adsorption on BFS is better for particle sizes corresponding to 300  $\mu\text{m}$ . Indeed, the adsorption rate regressed from 91.73% (300  $\mu\text{m}$ ) to 66.26% (500  $\mu\text{m}$ ) as the particle size increased. The increase in particle size resulted in the narrowing of the BFS

adsorption surface area, which caused the regression of the adsorption rate [32]. However, at particle sizes  $\Phi_s = 200 \mu\text{m}$ , the Pb (II) adsorption in solution on the BFS was found to be the least favourable (Fig. 3(b)). This result could be clarified, probably by the phenomenon of coalescence [33].

### 3.2.5. Effect of adsorbent dosage

The study of the impact of the adsorbent mass on the adsorption process is an essential step, since it informs us about the appropriate optimal mass.

From Fig. 4(a), it was observed that the adsorption rate increases with the mass of the adsorbent. This phenomenon can be explained by the increase in free active sites on the adsorbent surface [34]. Furthermore, it was observed that at high adsorbent masses ( $m > 1 \text{ g}$ ), the adsorption rate regresses slightly. The slight regression observed was probably caused by the agglomeration of slag particles from the blast furnace [35]. Accordingly, 1 g was selected as the optimum mass of adsorbent.

### 3.2.6. Effect of initial concentration

The initial concentration is a very important parameters in the Pb (II) adsorption process [36]. In this context, we have ranged the concentration from 10 to 80 mg/L (Fig. 4(b)).

The experimental data indicated that the adsorption capacity gradually increases up to a certain value, then it becomes constant (9.32 to 36.24 mg/g) (Fig. 4(b)). After 50 minutes of stirring, the maximum adsorption capacity of Pb (II) in solution on the BFS under optimal experimental conditions is 36.24 mg/g.



Fig. 3. a) Effect of temperature, b) Effect of particle size.





Fig. 4. a) Effect of adsorbent mass, b) Effect of initial concentration.

From equation 2, it has been noticed that the adsorption rate decreases with increasing initial Pb (II) concentration. This phenomenon can be explained by the inability of the surface of the solid at a constant number of sites to adsorb a quantity of ions in progression [37]. Moreover, it must be noted that a high initial concentration improves the diffusion of Pb (II) ions from the solution toward the adsorbent's active sites.

From the literature, it has been mentioned that the adsorption capacity of blast furnace slag is 53.58 mg of nickel per gram [22]. Blast furnace slag transformed into slag oxalate showed very good affinity for the adsorption of cobalt, where its maximum adsorption capacity is 576 mg/g [38]. Basic oxygen furnace slag showed good adsorption for a mixture of metal ions consisting of Cu, Cd, Pb, and Zn [39]. According to Table 2, BFS has a moderately acceptable adsorption capacity when compared to the adsorbents used in the processes for removing Pb (II) from solution.

### 3.3. Adsorption Isotherms

In the adsorption process, the interactions

between adsorbent and adsorbable are generally identified by mathematical models. In this study, Freundlich, Langmuir and Temkin [47] isotherm models used to fit the equilibrium adsorption data. The linear form of the models of Freundlich, Langmuir and Temkin are presented respectively by equations 3-6.

$$\log q_e = \log k + \frac{1}{n} \log C_e \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{q_{\max} b} \quad (4)$$

$$q_e = B_T \ln A_T + B_T \ln C_e \quad (5)$$

$$B_T = \frac{RT}{b_T} \quad (6)$$

Where  $q_e$  is the adsorbed amount (mg/g),  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>);  $K_F$  represents the Freundlich constant,  $n$  is the characteristic constant associated with the temperature,  $q_{\max}$  is the maximum capacity (mg/g) and  $b$  is the thermodynamic constant of the adsorption equilibrium (L.mg<sup>-1</sup>),  $A_T$  is Temkin isotherm equilibrium binding constant (L/g),  $b_T$  is Temkin isotherm constant,  $R$  universal gas constant (8.314 J/mol/K)  $T$  is temperature at 298 K, and  $B_T$  is Constant related to heat of sorption (KJ kmol<sup>-1</sup>).

Table 2. Comparison of uptake capacity of Pb(II) on various adsorbents

| adsorbent        | $q_{\max}$ (mg/g) | reference  |
|------------------|-------------------|------------|
| Zeolite          | 14                | [40]       |
| Oak wood ash     | 47.16             | [41]       |
| Green tea        | 100               | [42]       |
| Mangosteen peel  | 130               | [43]       |
| Tobacco leaves   | 24.7              | [44]       |
| Activated carbon | 22.8              | [45]       |
| Graphene oxide   | 36                | [46]       |
| BFS              | 34.26             | This study |

The parameters calculated from the models are represented in Table 3. The presentations of the models Freundlich, Langmuir, and Temkin are illustrated in Fig. 5. According to the results presented in table 3, the correlation coefficient of the Langmuir equation ( $R^2$ : 0.99) was higher than that of Freundlich ( $R^2$ : 0.83) and Temkin ( $R^2$ : 0.95). On the other hand, the maximum adsorption capacity calculated from the Langmuir model was closer to the measured value, which indicates that the Langmuir model is more appropriate for the Pb (II) adsorption on blast furnace slag in solution. This result allowed us to conclude that the Pb (II) adsorption in solution on the BFS was performed on a monolayer homogeneous surface.

The value of the Temkin model parameter ( $B_t$ ) indicates that the interaction between Pb (II) ions and BFS in solution is physical [47], and the value of the Freundlich model's heterogeneity factor ( $n$ ) indicates that adsorption is favorable [22] (Table 3).

The favorability of an adsorption process can be defined by the dimensionless separation factor ( $R_L$ ). Indeed, the  $R_L$  will classify the isotherm as either favorable ( $0 < R_L < 1$ ), unfavorable ( $R_L > 1$ ), or linear ( $R_L = 1$ ) [48].

$$R_L = \frac{1}{1 + C_0 b} \quad (7)$$

Where  $R_L$ : the Ratio indicates the quality of the adsorption,  $b$  is the Langmuir isotherm constant and  $C_0$  is the initial concentration.

Following the shape of the curve presented in Fig. 5(d), we have noticed the decrease in the value of the ratio  $R_L$  with the increase in the initial concentration and that this value was between 1 and 0, which allows us to conclude that the elimination of Pb (II) in solution on the BFS is favorable. Absolutely, this result confirms the previous hypothesis, where we mentioned the Freundlich parameter  $n$  ( $1 < n < 10$ ) [49]. Importantly, the  $R_L$  values revealed that as initial concentration increased, adsorption efficiency decreased.

### 3.4. Adsorption Kinetics

Kinetic study of the Pb (II) adsorption automatically involves the use of our experimental data in very widespread and well-established models. In this study, we have used three adsorption kinetics models to evaluate the adsorption process in this case: pseudo first order, pseudo second order, and internal diffusion [33]. The models exploited are represented respectively by equations 8-10.

The Lagergren model shows that the occupancy ratio of the adsorption site is directly proportional to the unoccupied ratio, which indicates that the adsorbed substance only binds to a single active site on the surface of the adsorbent. And the adsorption process is physical adsorption.

$$\ln(q_e - q) = -k_{Lag}t + \ln(q_e) \quad (8)$$

$$\frac{t}{q} = \frac{1}{k_b q_e^2} + \frac{1}{q_e} \quad (9)$$

$$q = k_w \sqrt{t} + C \quad (10)$$

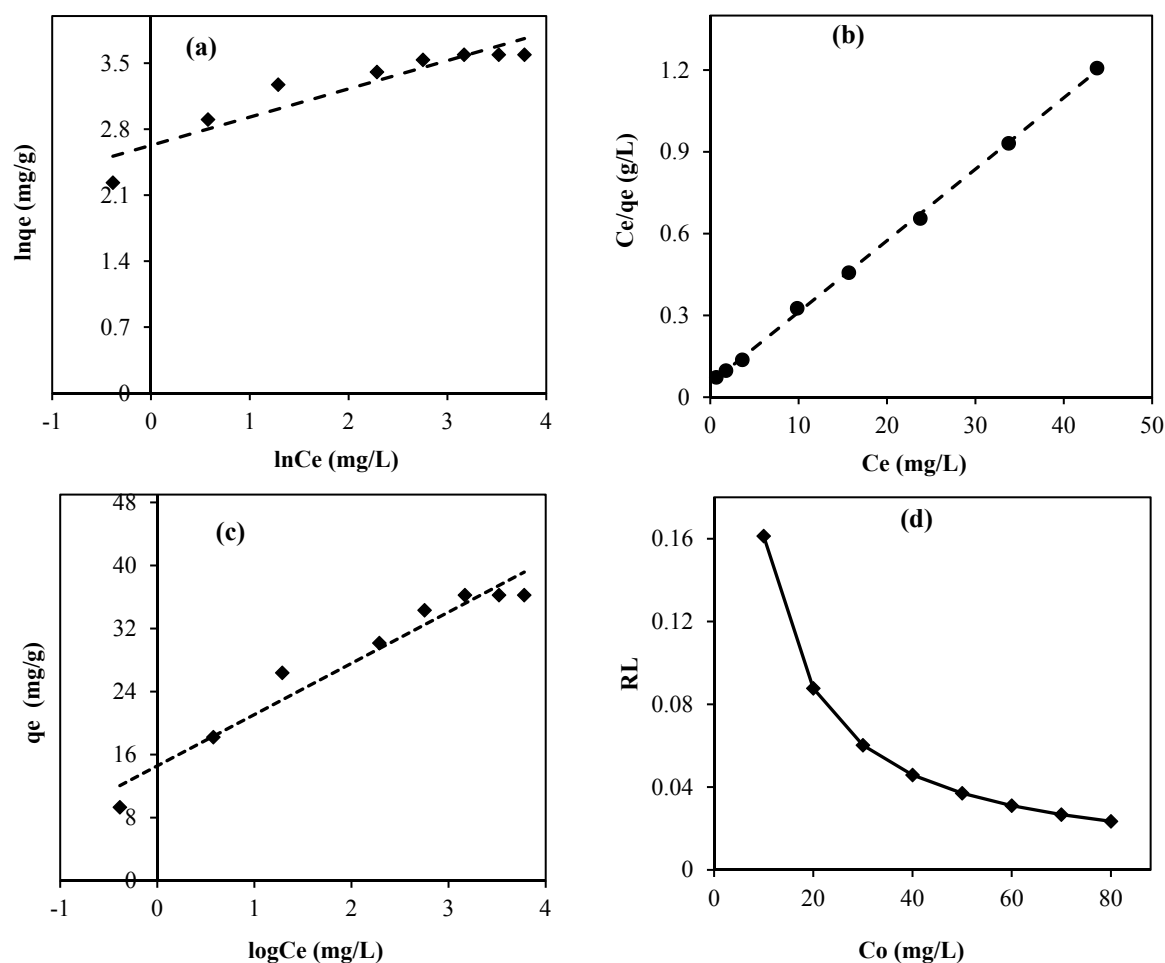
Where  $q_e$  is the adsorbed quantity at equilibrium (mg/g),  $q$  is adsorbed quantity at time  $t$  (mg/g),  $t$  is the time of adsorption process,  $k_{Lag}$  is the constant pseudo first order sorption speed ( $s^{-1}$ ),  $k_b$  is the constant of pseudo second order sorption speed ( $min^{-1}$ ),  $k_e$  is the coefficient of mass transfer through the outer film,  $C_0$  initial concentration (mg/L),  $C_e$  is the equilibrium concentration (mg/L),  $C_t$  is the concentration at time  $t$  (mg/L),  $k_w$  is the diffusion rate constant in the pores ( $mg/m \cdot min^{1/2}$ ) and  $C$  is the intercept and it's tied to the boundary layer.

The plot of  $\ln(q_e - qt)$  against time  $t$  was traced using the Lagergren equation Fig. 6(a) and the plot  $(t/qt)$  as a function  $t$  was traced using the Blanchard equation Fig. 6(b).

Based on the values in table 4, the pseudo second order model appears to be more appropriate for describing the Pb (II) adsorption process. In fact, the value of correlation coefficient  $R^2_{Blanchard} > R^2_{Lagergren}$  and the values of calculated adsorption capacity and experimental adsorption capacity are close [22]. S.-Y. Liu et al. [50] discovered the same result.

Table 3. Isotherm parameters Pb(II) adsorption by BFS.

| Freundlich | $K_F (mg \cdot g^{-1})(ml \cdot mg^{-1})^{1/n}$ | $n$                        | $R^2$ |
|------------|---|----------------------------|-------|
|            | 16.05   | 2.77                       | 0.86  |
| Langmuir   | $q_{max} (mg/g)$                                | $B (L \cdot mg^{-1})$      | $R^2$ |
|            | 38.46   | 2.77                       | 0.99  |
| Temkin     | $A_T (L/g)$                                     | $B_T (KJ \cdot kmol^{-1})$ | $R^2$ |
|            | 9.388   | 6.506                      | 0.95  |



**Fig. 5.** a) Presentation of Freundlich model, b) Presentation of Langmuir model, c) Presentation of Temkin model, d) Evolution of RL ratio as a function  $C_o$ .

From Fig. 6, it was shown that the plot of adsorbed capacity ( $q$ ) versus time ( $t$ ) has no intercept ( $C = 3.86$ ). Therefore, intraparticle diffusion is not the only mechanism that controls the adsorption process [51]. Indeed, Fig. 6(c) clearly depicts the various successive stages of Pb (II) diffusion from solution to adsorbent (BFS). In the first step, the Pb (II) was transferred from solution to the external surface of the BFS through film diffusion. In the second step, the Pb (II) gradually diffused from the surface of the BFS towards the internal pores. This process stops at equilibrium. Consequently, we deduce that the overall rate of Pb (II) adsorption in solution on BFS is controlled by two steps: the diffusion of the film on the outer surface and the intraparticle diffusion [52, 53].

### 3.5. Adsorption Thermodynamics

Thermodynamic parameters are very important,

because they shed precious insight into the nature of the metal ion adsorption process into solution. In this work, the variations in standard free energy ( $\Delta G^\circ$ ), standard enthalpy ( $\Delta H^\circ$ ), standard entropy ( $\Delta S^\circ$ ) and the distribution coefficient were employed to study the feasibility and spontaneous nature of the Pb (II) adsorption on into solution by BFS. These thermodynamic parameters are studied by involving the equations 11, 12 and 13 [54].

$$\Delta G^\circ = -RT \ln k_d \quad (11)$$

$$\ln k_d = \frac{\Delta H^\circ}{R} \times \frac{1}{T} + \frac{\Delta S^\circ}{R} \quad (12)$$

$$k_d = \frac{C_i - C_e}{C_e} \times \frac{V}{M} = \frac{q_e}{C_e} \quad (13)$$

By applying the function  $\ln(k_d) = f\left(\frac{1}{T}\right)$ , we found the straight line presented in Fig. 6(d). The regression analysis has indicated a good correlation ( $R^2 = 0.99$ ). The slope ( $1.111 \times 1000$ ) represents  $\frac{\Delta H^\circ}{R}$  and 3.369 corresponds at the intersection  $\frac{\Delta S^\circ}{R}$ .



Using equations 9, 10 and 11 we determined the thermodynamic parameters (Table 4).

From Table 4, it was observed that the values of the thermodynamic parameters, namely the free enthalpy variation ( $\Delta G$ ), enthalpy variation ( $\Delta H$ ) and entropy variation ( $\Delta S$ ) are negative.

The negative values of  $\Delta G$  indicate that the Pb (II) adsorption by BFS is spontaneous and feasible [26]. The decrease in the value  $\Delta G$  with increasing temperature reflects the adsorbent's high affinity for Pb (II) at 20°C. The negative

value of  $\Delta H$  indicates that the adsorption process is exothermic [55] and the low enthalpy value indicates that the adsorption process is physical ( $2 < \Delta H < 21$  kJ/mole) [25]. The fact that  $\Delta S$  value is negative indicates that during Pb (II) adsorption, the disorder at the solid/liquid boundary decreased [56].

The values of the free enthalpy ( $\Delta G < 20$  kJ/mole) show that the electrostatic interaction considerably influences the adsorption process of Pb (II) on the BFS [55].



**Fig. 6.** Adsorption kinetics and thermodynamics: a) Pseudo first order kinetic, b) Pseudo second order kinetic, c) Internal diffusion kinetic, d) Van't Hoff plot for nickel adsorption by BFS.

**Table 4.** Kinetic parameters of Pb(II) adsorption on BFS

|                           |                                |                                  |       |
|---------------------------|--------------------------------|----------------------------------|-------|
| <b>Lagergren model</b>    | $K_{lag}$ (min <sup>-1</sup> ) | $q_{e,theo}$ (mg/g)              | $R^2$ |
|                           | 0.105                          | 58.14                            | 0.93  |
| <b>Blanchard model</b>    | $K_b$ (g/mg min)               | $q_{e,theo}$ (mg/g)              | $R^2$ |
|                           | $9.05 \times 10^{-3}$          | 41.66                            | 0.98  |
| <b>Internal diffusion</b> | $C$ (mg/g)                     | $k_w$ (mg/g.min <sup>0.5</sup> ) | $R^2$ |
|                           | 3.86                           | 4.55                             | 0.95  |

**Table 5.** Thermodynamic parameters of the Pb(II) adsorption by BFS.

| Temperature (K) | $\Delta H$ (kJ/mole) | $\Delta G$ (kJ/mole) | $\Delta S$ (j/mole.K) | $K_d$ (L/g) |
|-----------------|----------------------|----------------------|-----------------------|-------------|
| 293             | -9.23                | -17.86               | -28.25                | 1.525       |
| 313             |                      | -18.46               |                       | 1.199       |
| 323             |                      | -18.75               |                       | 1.071       |

#### 4. CONCLUSIONS

In this research work, the Pb (II) adsorption on blast furnace slag (BFS) from aqueous medium was investigated as a function of contact time, initial pH, temperature, particle size and initial concentration. The physico-chemical characterization showed that the adsorbent consists mainly of the silica, lime, and alumina. The specific surface area of the BFS grains was around 275.8 m<sup>2</sup>/g. The zero point of charge (ZPC) corresponded to a pH of 3.8. The equilibrium time was reached after 50 minutes of agitation. Pb (II) adsorption capacity was 36.24 mg/g with an 87.93% yield under ideal experimental conditions ( $C_0$ : 60mg/L;  $V_{ag}$ : 150 rpm; pH: 5.4;  $\phi_s$ : 300  $\mu$ m, T: 20°C;  $M_s$ : 1 g). The adsorption capacity declined with increasing temperature, indicating that lead adsorption is better at low temperatures (20°C). Modeling of the experimental data revealed that the Langmuir model was better suited to describe the isothermal behavior than the Freundlich and Temkin models. Which demonstrates that the lead removal process took place on a homogeneous monolayer surface. The kinetic studies revealed that the Pb (II) adsorption process was well fitted by pseudo-second order, with an  $R^2 = 0.98$  correlation coefficient. The mechanism of the transfer of Pb (II) ions from solution to BFS surface was studied, and it was discovered that the overall rate of adsorption was controlled successively by external diffusion and intraparticle diffusion. The thermodynamic study revealed that the elimination of Pb (II) on the BFS is spontaneous, exothermic, less entropic, and physical in nature, and the adsorption of Pb (II) is done by the electrostatic interaction. Finally, BFS can be used as a reliable and efficient adsorbent for Pb (II) elimination removal from waste water.

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