



ORIGINAL RESEARCH ARTICLE

Response surface modeling and optimization of lead uptake from aqueous solution by porous graphitic carbon synthesized from Egyptian bituminous coal

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Received for publication: May 10, 2016; Accepted: May 25, 2016

Abstract: El Maghara bituminous coal, collected from northern Sinai, Egypt, was used as a precursor material in the synthesis of porous graphitic carbon by chemical and thermal treatment. The activation process was carried out using phosphoric acid followed by thermal treatment at 800°C in an electric muffle furnace for 1h. The raw coal and the synthetic porous carbon were characterized by polarized light microscope (PLM), XRD, SEM and FTIR. Experiments were conducted based on a central composite rotatable statistical design (CCRD) and analyzed using response surface methodology (RSM). The sorption process was investigated as a function of four independent parameters, initial solution pH (2–7), initial lead concentration (50–150 mg/l), contact time (30–240 min) and porous carbon dose (0.1–0.5 g). According to the F-values, the second order polynomial model was found to be highly significant for lead uptake with only a 0.01% noise. Also, the matching between the actual and the predicted results ($R^2 > 0.98$) reflects the suitability of the design to represent the sorption process. The experimental optimum conditions for the uptake of lead by the porous carbon at pH 4 were found to be 120 min, 50 mg/L, 0.3 g for contact time, initial concentration and adsorbent mass, respectively. By studying the effect of the selected parameters and the interaction between them, the applied model can enhance the adsorbed amount of lead (q_e) and the removal efficiency (%) through a series of suggested solutions.

Key words: Bituminous coal; Synthetic porous carbon; Experimental parameters; Statistical design.

Introduction

The discharge of heavy metals into water bodies leads to serious problems to human health and environment. Small amounts of naturally occurring heavy metals such as zinc (Zn), copper (Cu), lead (Pb) and cobalt (Co) are common in our environment and they are necessary to our health (Qiu and Zheng, 2009). However, the high concentrations of these heavy metals are dangerous for living organisms due to their toxicity, stability and tendency to accumulate in the environment (Kragovic, *et al.*, 2013). The accumulation of heavy metals over time in human bodies can cause severe damage of kidney, liver, reproductive system, lungs, blood composition and sometimes leads to cancer (Jamil, *et al.*, 2010).

Lead is widely used in many industries such as storage battery, printing pigment, fuels, and photographic materials (Jalali *et al.*, 2012). Releasing of lead to the surround environment and its accumulation in the human body can cause many diseases such as impaired blood synthesis, hypertension, severe stomach ache, brain, kidney damage and even miscarriage in pregnant women (Jeyakumar and Chandrasekaran, 2014). According to the World Health Organization (WHO), the maximum permissible level of lead in drinking water is 0.1 mg/L since lead is cumulative poison (Saleh *et al.*, 2013). Chemical precipitation, ion exchange, neutralization, reduction and adsorption are used as different processes to uptake heavy metals from contaminated water (Abukhadra *et al.*, 2015). Removal of heavy metals by adsorption process is

preferred because it is very effective, economic, versatile and simple (Zhu, *et al.*, 2013, Seliem *et al.*, 2015).

Porous carbons were recommended as adsorbent materials with high capacities because of their well-developed internal pore structure, high surface area and the presence of a wide spectrum of surface functional groups in the carbon matrix (Chingombe *et al.*, 2005). Adsorption characteristics of the porous carbons are controlled by both the nature of the precursor material and the method of activation process (Lua and Gua, 2001). Chemical activation is performed by carbonizing the precursor in the presence of a chemical agent such as H_3PO_4 and KOH and it gives high amounts of porous carbons as compared to physical activation (Kopac and Topark, 2007). Porous carbons can be synthesized from many raw materials such as coal, wood, corn, petroleum, peat and other biomass (Kopac and Topark, 2007). Coal is the most commonly used precursor in the preparation of porous carbons due to its availability and low price (Hsu and Teng, 200). The coal based porous carbon has some specific beneficial properties such as well-developed surface area, high chemical and mechanical resistance, ease of degradation, good ion exchange properties, high density, corrosion resistance, hardness and durability (Pietrzak *et al.*, 2006).

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are used for analyzing the influence of different

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independent parameters on the response (Amini *et al.*, 2008). The experimental design techniques commonly used for process analysis and modeling are the full factorial, partial factorial and central composite rotatable designs. Central composite rotatable design (CCRD) has been shown to be sufficient to describe the majority of steady-state process responses (Xing-dong *et al.*, 2013).

To optimize the heavy metals uptake, changing the independent parameter such as contact time, adsorbent mass, initial concentration, and solution pH, is required with keeping all the other parameters constant. These changes consume time and money as well (Ghorbani *et al.*, 2008). Therefore, the application of the RSM is very important to save cost and time by predicting the conditions at which optimization occurred. Also the application of RSM evaluates the interactive effects of the different independent parameters and their impact on the heavy metal removal process (Bas and Boyaci, 2007). El Maghara coal deposits, located at northern Sinai, are the largest and the only economical coal deposits in Egypt (Al-Far, 1966). The Ministry of Petroleum and Mineral Resources in 2011 pointed out that the proven reserve of the mine is about 25 million tons of coal, while the probable geological reserve is about 50 million tons, but unfortunately such deposits have not been exploited for industrial and environmental applications so far. Thus, the aims of this study were: (1) to synthesize graphitic porous carbon from bituminous coal of El Maghara area, (2) to characterize the raw coal and the prepared porous carbon, (3) to use the Response Surface Methodology (RSM) in conjunction with the Statistical Central Composite Rotatable Design to study the effect of the selected parameters and the interaction between them on the adsorption process and (4) to use the CCRD of second order quadratic polynomial model to obtain the optimum conditions for the removal of lead by the synthetic porous carbon.

Material and Methods

Materials: Coal samples, collected from El Maghara coal mine, were used as a starting material for the synthesis of porous carbon. The used chemicals hydrofluoric acid (HF, 42%), hydrochloric acid (HCl, 98%) and phosphoric acid (H₃PO₄, 85%) were purchased from Sigma-Aldrich. Lead stock solution (1000 mg/L) was supplied by Sigma-Aldrich. The different concentrations of lead were prepared by diluting the stock solution with distilled water.

Synthesis of porous carbon: Coal samples were grounded by agate mortar and screened by 100 μ m sieve; 100 μ m fractions were collected for the activation processes. The precursor coal was treated by aqueous solutions of 20% HCl and 25% HF for 2h at 60°C to reduce the ash content, followed by filtration and washing by distilled water several times

to remove any traces of fluoride or chloride ions. The chemically treated coal sample was oxidized in open atmosphere at 120°C for 24h to avoid the plastic effect of the present resinous materials and then, carbonized at 500°C for 2h. A 5g of the carbonized coal was mixed with 50 ml solution of phosphoric acid. The mixture was homogenized by magnetic stirrer for 3h at 100 rpm and dried by a vacuum dryer at 100°C for 24 h. The acid treated coal was thermally activated at 800°C for 1h in an electric muffle furnace. After cooling, the activated product was washed by 0.5N NaOH solutions, followed by filtration and washing the solid product by hot distilled water several times until pH 7. Then the product was dried at 100°C for 24 h and kept for characterization.

Characterization

Complete chemical analysis for the raw coal sample was carried out throughout proximate and ultimate analysis (ASTM, 1984 and ISO 331, 1975). Petrographical investigation was performed using Nikon polarized light microscope. Morphology of the original sample and the synthesized porous carbon was studied by a field emission scanning electron microscope (JSM-6510, JEOL, Tokyo, Japan). X-ray powder diffraction patterns of the raw and the treated products were carried out using a Philips APD-3720 diffractometer with Cu K α radiation, operated at 20mA and 40 kV in the 2 θ range of 5–70 at a scanning speed of 5°/min. Fourier transform infrared analysis (FTIR-8400 S Shimadzu, Japan) was used in order to determine the change in the chemical structural of the Maghara coal sample after activation.

Statistical modeling and optimization

CCRD of second order quadratic polynomial model was designed for four selected parameters (contact time, initial concentration, pH and dose of porous carbon) to detect the effect of such parameters in the adsorption of lead and to predicted the optimum removal conditions of lead. The experiments were performed according to the tests suggested by the applied statistical design. A 100ml of the suggested prepared solutions was shaken by orbital shaker with the suggested dosage for different contact times and at different pH values. The pH values were adjusted using sodium hydroxide solution (0.1N) and nitric acid solution (0.1N). At the end of each time interval, the solid and liquid was separated by filtration using Whatman 45 μ m pore size filter paper. The pH values for the solutions re-adjusted to be acidic by using dilute nitric acid. Then, solutions were collected in clean vials and the concentrations of lead in all solutions were determined by using inductively coupled plasma mass spectrometry (ICP-MS). The upper and lower limits of the selected variables in the actual and coded values set in (Table 1).

Table 1: The upper and lower limits of the selected variables in the actual and coded values used for removal of lead from aqueous solution.

Factor	Name	Low actual	High actual	Low coded	High coded
A	Contact time	30 min	240 min	-1	1
B	Initial concentration	50 mg/L	150 mg/L	-1	1
C	Dosage	0.1 gm	0.5 gm	-1	1
D	PH	2	7	-1	1

The amount of adsorbed lead ions onto the porous carbon q_e (mg/g) and the removal efficiency (%) were calculated as follows:

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

$$\text{Removal efficiency (\%)} = \frac{100(C_0 - C_e)}{C_0}$$

Where C_0 and C_e are the lead concentrations in the initial solution and the solution after equilibrium, respectively. V is the volume of solution in (L) and m is the mass of sorbent (g). The data obtained were fitted to a second-order polynomial equation:

$$Y = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \beta_{ii} X_i^2 + \sum_{i=1}^3 \sum_{j=i+1}^4 \beta_{ij} X_i X_j$$

Where Y is the required responses (the amount of adsorbed lead (q_e) and the removal efficiency of lead (%)); β_0 , β_i , β_{ii} , β_{ij} are constant coefficients, X_i are the uncoded independent variables. Subsequent regression analyses, analyses of variance (ANOVA) and response surfaces were performed using the Design Expert Software (Version 6.0.5). Optimal reaction parameters for maximum removal were generated using the software's Numerical Optimization Function.

Results and Discussion

Proximate and ultimate analyses and PLM results: Proximate and ultimate analyses revealed that, El Maghara coal deposits are characterized by 38.6% fixed carbon, 51.39% volatile matters and 7367 k cal/ kg calorific value indicating that the coal deposits are of high volatile bituminous rank with low to medium grade and of low ash content 5.26% (Table 2).

Table 2: Proximate and ultimate analyses of the original coal sample.

Proximate analysis of El-Maghara coal	
Constituent	Wt., %
Moisture	2.12
Ash	5.26
Volatile Matter	51.39
Fixed carbon	38.6
Total sulfur	2.9
Calorific value	7367 k cal/kg
Hardgove Index	44
Swelling Number	2-2.5
Ultimate analysis of El-Maghara coal	
Constituent	Wt., %
Carbon	41.04
Hydrogen	6.11
Nitrogen	91.27
Oxygen	10.45
Sulfur	2.70-3.20

Petrographical investigation by polarized light microscope showed that vitrinite with red or reddish black color is the most abundant macerals (Fig.1A) in El Maghara coal (nearly 90%). Liptinites are represented by pollens, spores, resinous materials and cuticles (Fig. 1B and C) at a percentage of about 8% from the present macerals. Inertinite is not common and appears as fusinite with its cellular texture. The cell's cavities of fusinite are filled with opaque minerals mainly pyrite. Ashes are represented by quartz and framboidal pyrite (Fig.1D).

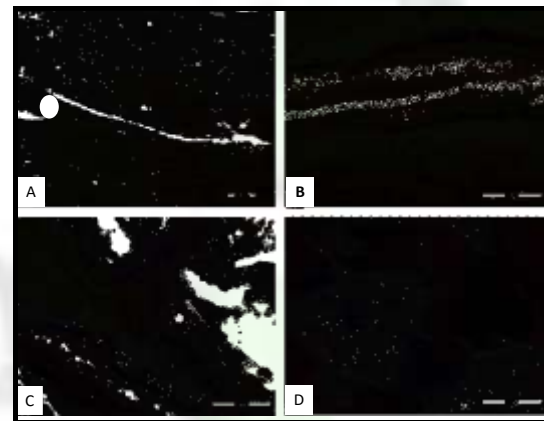


Fig. 1: PLM images of (A) general view for the coal macerals where the vitrinite (brownish in color) is the main macerals (arrows refer to pollens (liptinite within vitrinite), (B) Resinous materials filling canals within the coal sample, (C) Cuticle liptinite within the coal and (D) Pyritic impurities surrounded by cryptocrystalline silica.

XRD, FTIR and SEM results

The XRD patterns of the raw coal, acid leached coal and the synthetic porous carbon are shown in (Fig.2). The coal samples showed a broad peak centered at 2θ value of 15° indicating the predominance of amorphous carbon structure (Fig. 2). The synthetic porous carbon gave intense and narrow diffraction peaks at 2θ values of 14.85° , 22.95° , 24.08° , 26.54° and 43.57° . Such peaks correspond to the crystalline graphite peaks with its characteristic main peaks (Mopoung, 2011).

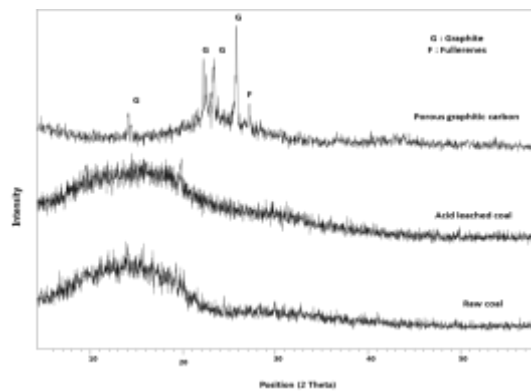


Fig. 2: XRD patterns of raw coal, acid leached coal and the synthetic porous carbon.

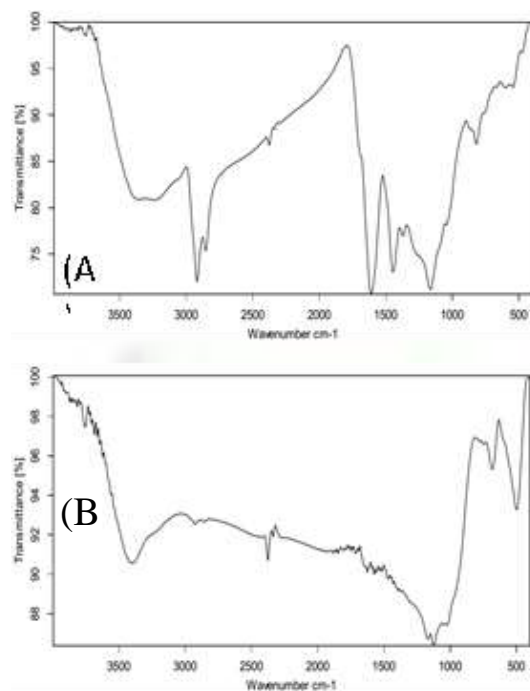


Fig. 3: FT-IR spectra of the raw coal (A) and the prepared porous carbon (B)

FT-IR spectra for the raw coal and the synthetic porous graphitic carbon are depicted on (Fig.3). It was indicated that the raw coal sample exhibited noticeable IR bands (Fig.3A). Broad band from 3000 to 3500 cm^{-1} is attributed to the O-H stretching vibration of surface hydroxylic groups as well as to the adsorbed water (Manoj *et al.*, 2009). The band at 2900 cm^{-1} is assigned to aliphatic asymmetrical $-\text{CH}_2$ stretching, the band at 2854 cm^{-1} is for aliphatic symmetrical $-\text{CH}_2$ stretching, the small band at about 2320 cm^{-1} related to ketone group, band at 1610 cm^{-1} is assigned to $\text{C}=\text{C}$ stretching conjugated with another $\text{C}=\text{C}$ bond, an aromatic nucleus, or a $\text{C}=\text{O}$ bond. The band at 1447 cm^{-1} is attributed to plane bending vibration of C-H of methylene group while the IR band which appears at 1372 cm^{-1} is related to plane bending vibration of C-H in methyl group (Budinova *et al.*, 2006). Other bands appear in the FT-IR pattern of raw coal sample represented by broad band between 1000 and 1200 cm^{-1} which is

assigned to C-O stretching in phenols, alcohols, acids, ethers and esters (Puziy *et al.*, 2003). The bands between 600 and 900 are related to plane deformation vibration of C-H groups located at the edges of aromatic planes (Manoj *et al.*, 2009). After the graphitization process the absorption bands are reduced to two main broad peaks (Fig.3B). The first one is between 3400 and 3500 cm^{-1} where the second is between 1000 and 1200 cm^{-1} . These peaks are corresponding to O-H and C-O stretching vibrations, respectively. Moreover, there is small absorption bands at 2380 cm^{-1} for the ketone group, 1586 cm^{-1} for the carbonyl group and bands between 500 and 900 are ascribed to aromatic.

The SEM images for the raw coal and the synthetic active carbon are illustrated in (Fig. 4). The morphology of the raw sample appears to be mainly flaky coal grains of different sizes (Fig.4A). However, the synthetic porous carbon shows flaky appearance with porous structure (Fig.4B).

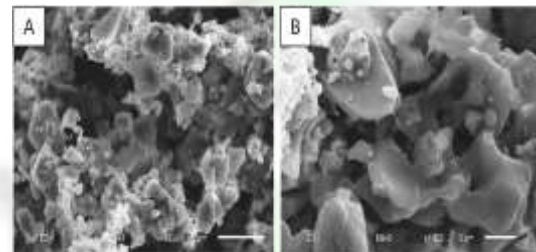


Fig. 4: SEM images of (A) the raw coal and (B) the synthetic porous carbon.

Statistical molding

Table 3 summarizes the experimental runs designed with the CCRD for removal of Pb^{2+} from aqueous solution using the synthetic porous carbon in terms of independent variables (contact time, initial concentration, adsorbent dosage and pH) and the resulted responses Pb^{2+} uptake (mg/g) and removal efficiency (%). The normal probability plot of studentized residuals for the two responses is shown in Fig.5. The plot showed that the data are approximately normal for (Pb^{2+} uptake (mg/g) and removal efficiency, % (Fig.5A and B, respectively).

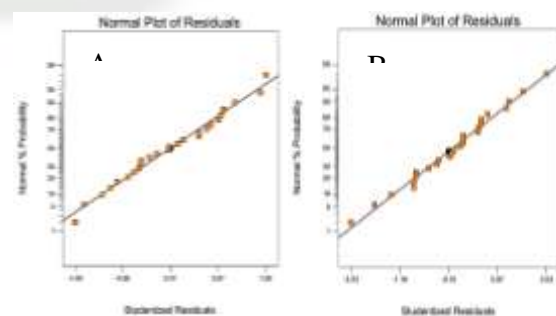


Fig. 5: Normal plot of the studentized residuals for (A) amount of lead uptake (mg/g) and (B) Removal of lead (%).

Table 3: Results of the experimental runs designed according to the CCRD for lead uptake

Run	Contact time (A)	Initial concentration (mg/L) (B)	Dosage (C)	pH (D)	Uptake (mg/g)	Removal efficiency (%)
1	30.00	150.00	0.10	2.00	47.1	31.4
2	30.00	50.00	0.50	2.00	8.95	89.5
3	240.00	50.00	0.10	2.00	27.65	55.3
4	30.00	50.00	0.10	2.00	24.95	49.9
5	120.00	100.00	0.10	4.00	52.9	52.9
6	240.00	150.00	0.50	2.00	19.4	63.8
7	120.00	100.00	0.50	4.00	19.06	95.3
8	240.00	50.00	0.10	7.00	30.2	60.4
9	240.00	150.00	0.10	2.00	60.45	40.3
10	30.00	50.00	0.10	7.00	26.25	52.5
11	120.00	150.00	0.30	4.00	33.7	67.4
12	30.00	50.00	0.50	7.00	9.38	93.8
13	240.00	150.00	0.50	7.00	21.48	71.6
14	240.00	150.00	0.10	7.00	68.1	45.4
15	30.00	150.00	0.10	7.00	55.1	36.7
16	30.00	150.00	0.50	2.00	17.94	59.8
17	120.00	100.00	0.30	4.00	25.6	76.8
18	120.00	100.00	0.30	2.00	16.73	50.2
19	240.00	50.00	0.50	2.00	9.76	97.6
20	120.00	100.00	0.30	7.00	22.1	66.3
21	30.00	150.00	0.50	7.00	18.63	62.1
22	30.00	100.00	0.30	4.00	24.53	73.6
23	240.00	50.00	0.50	7.00	9.92	94.6
24	120.00	50.00	0.30	4.00	16.35	98.1
25	240.00	100.00	0.30	4.00	25.58	76.75
26	120.00	100.00	0.30	4.00	25.6	76.8

Fitting of the statistical model

Second order quadratic polynomial model was selected to represent the relations between the selected parameters and the required responses. The analysis of variance (ANOVA) of the second order polynomial models revealed that, the Model F-values are 92.8 and 54.62 for the amount of lead adsorbed (q_e) and the removal of Pb^{2+} (%) respectively. According to the F-values, the model is highly significant with only a 0.01% noise. Pure errors are zero which indicates a very good reproducibility of the obtained data. The mathematical equations of the quadratic polynomial model, which represent the relations between the required responses (amount of lead uptake by porous carbon (q_e (Y1)) and removal efficiency of lead % (Y2)) and the selected variables, were obtained from Design Expert Software (Version 6.0.5) for coded units as follows:

$$Y1 = + 26.57 + 2.21 X A - 14.39 X B + 1.57 X C + 9.96 X D - 0.94 X A^2 + 10.31 X B^2 - 6.84 X C^2 - 0.64 X D^2 - 1.66 X A X B + 0.15 X A X C + 1.43 X A X D - 0.93 X B X C - 5.14 X B X D + 0.90 X C X D$$

$$Y2 = + 77.88 + 3.40 X A + 17.10 X B + 2.79 X C - 12.08 X D - 1.15 X A^2 - 1.73 X B^2 - 18.88 X C^2 + 6.92 X D^2 - 0.32 X A X B + 0.27 X A X C + 0.32 X A X D - 0.23 X B X C - 3.66 X B X D + 0.51 X C X D$$

Actual removal efficiency of Pb^{2+} obtained by the experimental tests and the predicted results by using the model equations are given in Table 4. The predicted results showed great agreement with the actual results with high determination coefficients $R^2 = 0.9916$ and 0.9858 for lead adsorption and the removal efficiency, respectively (Fig.6A and B). This

indicated the significance of the quadratic polynomial model and its suitability to represent the actual relations between the required responses and the selected variables.

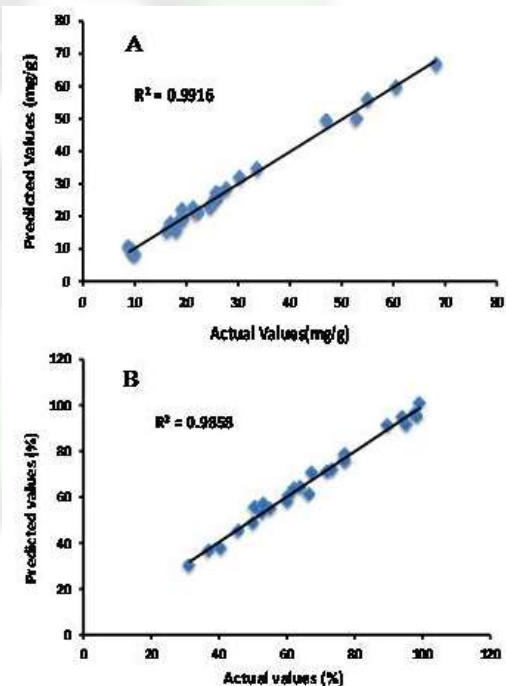


Fig. 6: The R^2 values for the amount of lead adsorption (mg/g) (A) and the removal efficiency of lead (%) (B).

Table 4: The experimental tests and the predicted results by using the model equations

Amount of lead uptake (mg/g)		Removal efficiency (%)	
Actual values	Predicted values	Actual values	Predicted values
24.95	23.85	49.90	48.75
27.65	28.42	55.30	54.99
8.95	10.53	89.50	91.35
9.76	8.48	97.60	96.32
26.25	26.78	52.50	53.24
30.20	31.94	60.40	60.56
9.38	9.72	93.80	94.91
9.92	8.26	99.20	100.97
47.10	49.39	31.40	30.23
60.45	59.69	40.30	37.76
17.94	15.51	59.80	58.20
19.40	19.19	63.80	64.47
55.10	55.90	36.70	36.76
68.10	66.79	45.40	45.37
18.63	18.28	62.10	63.80
21.48	22.55	71.60	71.15
24.53	22.86	73.60	72.07
25.58	27.22	76.75	78.76
52.90	49.93	52.90	57.16
19.06	22.00	95.30	91.53
16.73	17.85	50.20	55.74
22.10	20.95	66.30	61.25
16.35	15.43	98.10	95.23
33.70	34.58	67.40	70.76
25.60	25.65	76.80	76.07
25.60	25.65	76.80	76.07

Effect of the selected Parameters on lead uptake

The influence of the selected parameters on the removal of lead by the synthetic porous graphitic carbon was expressed in linear response surface diagram (Fig.7).

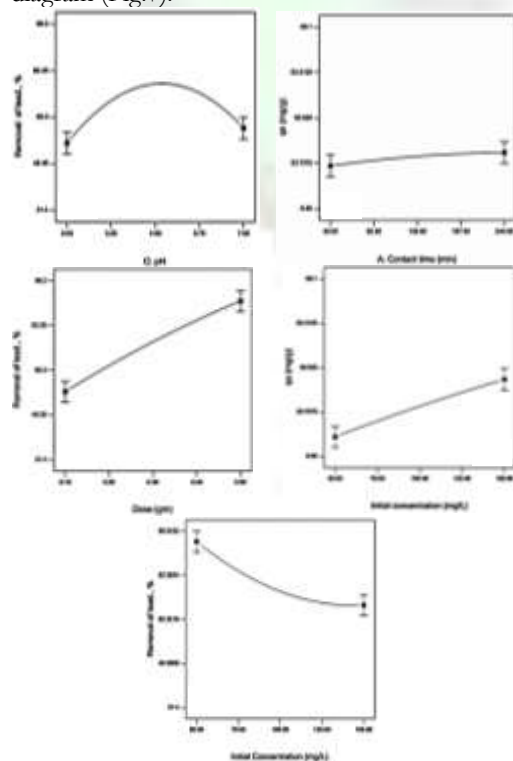


Fig. 7: The influence of the selected parameters on the removal of lead by the synthetic porous graphitic carbon (A) the effect of pH on removal efficiency of lead, (B) The effect of contact time on the removed

amount of lead (C), the effect of dose on removal efficiency of lead, (D), the effect of initial concentration on the removed amount of lead and (E) the effect of initial concentration on removal efficiency of lead.

Effect of pH

The pH of aqueous solution is a critical factor controlling the metal speciation, degree of ionization as well as the surface properties of the adsorbent material which in turn can affect the extent of adsorption (Karthikeyan *et al.*, 2008). The influence of pH on the adsorption of lead onto the porous graphitic carbon was investigated using the statistical analysis of the CCRD in the pH range from 2 to 7 at room temperature. The results of pH effect, with keeping the other parameters constant at (120 min of contact time, 0.3 g of adsorbent dose and 100mg/L of initial lead concentration), were plotted in linear response surface diagram (Fig.7A). As can be seen, the adsorption of lead by the porous carbon was low at $\text{pH} < 4$ and increased to the maximum value at the pH range from 4.5 to 5. By increasing the pH of the solution above 5, the removal efficiency of lead decreased. The previous results are based on the fact that at pH range between 2 and 3, hydrogen ions compete with lead ions on the surface of the porous carbon which impend reaching the lead ions to the active sites of the sorbent due to the repulsive forces (Saleh *et al.*, 2013).

With increasing pH value from 4 to 5, more ligands such as amino, phosphate and carboxyl groups would be exposed and carry negative charges with subsequent attraction of metal ions (Aksu, 2001). Therefore, the negative charges on the surface of the porous carbon favor the adsorption of Pb^{2+} through electrostatic force of attraction (Jeyakumar and Chandrasekaran, 2014). At higher pH values above 5, the speciation diagram of lead shows that other species of lead such as $[\text{Pb}(\text{OH})]^+$, $[\text{Pb}_3(\text{OH})_4]^+$, and $[\text{Pb}(\text{OH})_2]$ tend to be produced in the solution (El-Waki *et al.*, 2014).

Effect of contact time

The influence of contact time on the adsorption processes was investigated at fixed pH 4, initial concentration 100 mg/L and dose 0.3 gm. The relation was plotted in linear response surface graph (Fig.7B). As can be seen, the adsorption of lead ions by porous graphitic carbon showed two distinct stages with different slopes. The first stage at contact time ($30 < t < 120$ min) was characterized by a steep slope due to the rapid adsorption rate. At this initial stage, the removal efficiency of lead increased from 73.6% to 76.8%. By increasing the contact time from 120 min to 240 min, at the final stage, the removal percentage of lead was nearly constant, i.e. equilibrium was attained. Equilibrium was achieved due to the decreasing in the available active adsorption sites on the porous carbon and therefore,

transfer of the lead ions from solution to the external surface of adsorbent became limited (Seliem *et al.*, 2015). This stage was signified by a gentle slope as a result of decreasing the adsorption rate of lead by the synthetic porous carbon (Seliem *et al.*, 2013).

Effect of adsorbent dose

The effect of the porous graphitic carbon mass on the adsorption processes was investigated at fixed pH 4, initial concentration 100 mg/L and contact time 120 min. (Fig. 7C). Response surface graph revealed that the removal efficiency of lead increased from 52.9% to 95.3% with increasing the mass of the porous carbon from 0.1g to 0.5 g. This was expected due to the increase in the available surface area and the number of active sites of adsorbent (Seliem *et al.*, 2016).

Effect of initial concentration

The influence of initial lead concentration on the adsorption processes was investigated at fixed pH 4, dose 0.3 gm and contact time 120 min (Fig.7D and E). The amount of adsorbed Pb^{2+} increased from 16.35 mg/g to 33.7 mg/g with increasing the initial concentration from 50 mg/L to 150 mg/L, respectively (Fig.7D). On the other hand, the removal efficiency decreased from 98.1% to 67.4% with increasing the initial lead concentration from 50 mg/L to 150 mg/L, respectively (Fig.7E). The initial concentration may provide the driving force to overcome the resistance of the mass transfer of Pb^{2+} between liquid and solid phases (Aroua *et al.*, 2008). The initial concentration was as high as the driving force, therefore the adsorption capacity increased (El-Waki *et al.*, 2014).

Interaction effect of the selected parameters on lead uptake

The interaction results can provide a good substrate on which the predicted optimum conditions can be detected. 3D response surface diagrams represent the interaction between the selected parameters are given (Figs 8 and 9). Elliptical shape of the curve indicates a good interaction of any two variables while circular shape indicates no interaction between them (Mohamed *et al.*, 2015). The interaction effect between the operating parameters can be obtained by plotting of two parameters with maintaining values for the other parameters.

Effect of interaction between contact time and initial pH on lead uptake

The interaction effect between pH and the other operating parameters are represented in 3D response surface diagrams (Fig.8). At pH 4, the amount of adsorbed lead (q_e) (100 mg/L of initial concentration and 0.3g of dose) slightly increased with increasing the contact time from 24.53 mg/g after 30 min to 25.58 mg/g after 240 min (Fig.8A). Also, the adsorption capacity at certain contact time is controlled by the solution pH values. At 30 min of

contact time, the amount of adsorbed lead increased from 15.15 mg/g to 23.42 mg/g with increasing pH from 2 to 5, respectively. Therefore, the optimum condition for lead uptake is at pH range from 4 to 5.

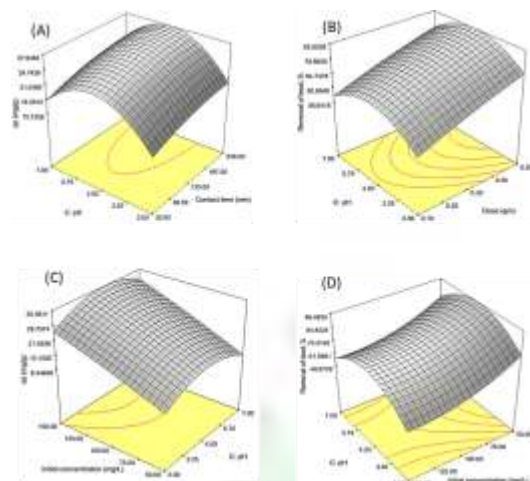


Fig. 8: Interaction effects between pH and the other operating parameters, (A) pH with contact time, (B) pH with dose, (C and D) effect of pH with initial concentration on the removed amount of lead and the uptake efficiency of lead, respectively.

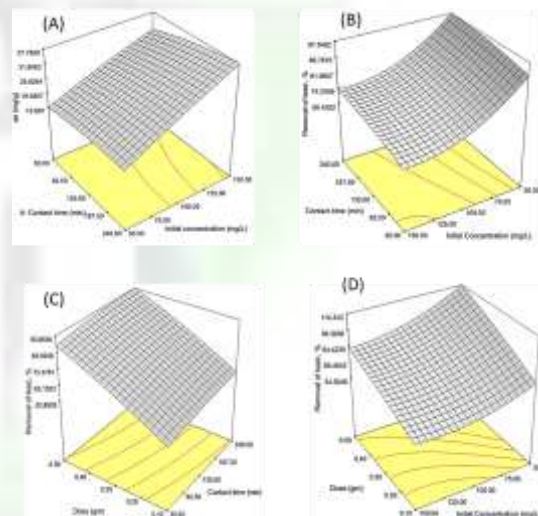


Fig. 9: Interaction effects between contact time, dose and initial lead concentration on the % uptake of lead.

Effect of interaction between porous carbon dose and pH on lead uptake

At pH 4, the removal of Pb^{2+} % at contact time 120 min and initial concentration 100 mg/L recoded the maximum value (95.3%) at the maximum value of dose (0.5 g) while at the minimum value of the dose (0.1g) the removal efficiency gave a value of 52.9% (Fig.8B). As can be seen, the best operating pH is between 4 and 5.

Effect of interaction between initial concentration and pH on lead uptake

The influence of interaction between pH and initial lead concentration on the removed amount of lead (q_e) and the removal efficiency of lead (%) is represented (Fig.8 C and D). At pH 4, contact time 120 min and dose 0.3 g, the amount of lead uptake by porous graphitic carbon increased from 16.35 mg/g at the lower limit of the initial concentration (50 mg/L) to 33.7 mg/g at the upper limit of concentration (150 mg/L), while the removal of lead% decreased from 98.1% at the lower limit to 67.4% at the upper limit. Also the optimize pH at any certain concentration is between 4 and 5.

Effect of interaction between Contact time and concentration on lead uptake

The interaction effect reveal that, at time 120 min, dose 0.3 gm and pH 4, the adsorption capacity increased from 16.35 mg/g to 33.7 mg/g by increasing the initial concentration from 50 mg/L to 150 mg/L, respectively (Fig.9A and B). As shown in Fig. 9A, the best contact time for the maximum removal of Pb^{2+} ions at a certain concentration is 120 min.

Effect of interaction between contact time and dose on lead uptake

The interaction between contact time and dose on lead uptake revealed that best removal efficiency at certain time is achieved at the upper limit of dose (0.5 g), where the 120 min contact time is still the best contact time at any given dose (Fig. 9C).

Effect of interaction between concentration and dose on lead uptake

The interaction between the initial concentration and the porous carbon dose appear in Fig (9D). The adsorbent material exhibited the best results at the lower limit of concentration (50 mg/L) at 0.5 g of adsorbent dose.

Optimization

The experimental runs revealed that the best removal efficiency (98.1%) for lead was obtained at run 24, contact time 120 min, 50 mg/L initial concentration, 0.3 gm dose and pH 4 (see Table 3). By using the Design Expert's Optimization Function, the optimum experimental results can be enhanced through a series of predicted optimum solutions. These enhancements are governed by the upper and lower limits for the optimizing process (Table. 5). The predicted optimum solutions are given in Table 6 and can be summarized as the follow (Fig. 10):

- Solution 1, a combination of 66 min contact time, 0.42 g dose and pH 4.6 can completely remove about 50 mg/L of lead solution (Fig.10A).
- Solution 2, a combination of 78 min contact time, 0.48 dose, the predicted capacity increased to completely remove about 67 mg/L of lead at pH 4.7 (Fig.10B).
- Solution 3, a combination of 120 min contact time, 0.49 g dose at pH 4.5, 80 mg/L of lead solution is predicted to be removed by the porous carbon (Fig.10C).
- Solution 4, a combination of 122 min contact time, 0.47 g dose, pH 4.5 can remove about 76 mg/L of lead ions from the solution (Fig. 10D).

Table 5: Optimization test scheme constraints for the removal of Pb^{2+} using porous graphitic carbon.

Name	Goal	Lower Limit	Upper Limit	Lower Weight	Upper Weight	Importance
Contact time	Is in range	30 min	125 min	1	1	3
Initial concentration	Is in range	50	150	1	1	3
Dose	In the range	0.1	0.5	1	1	3
pH	In the range	4.5	5	1	1	3
Removal of Pb^{2+} , %	Maximize	31.4	98.1	1	1	3

Table 6: The suggested solutions for maximum removal of Pb^{2+} ions using porous carbon.

Number	Contact time (min)	Initial concentration (mg/L)	Dose (gm)	PH	Removal efficiency (%)	Desirability
1	66	52	0.42	4.6	100	1
2	78	67	0.48	4.7	100	1
4	120	79	0.49	4.5	100	1
5	122	76	0.47	4.5	99.34	1

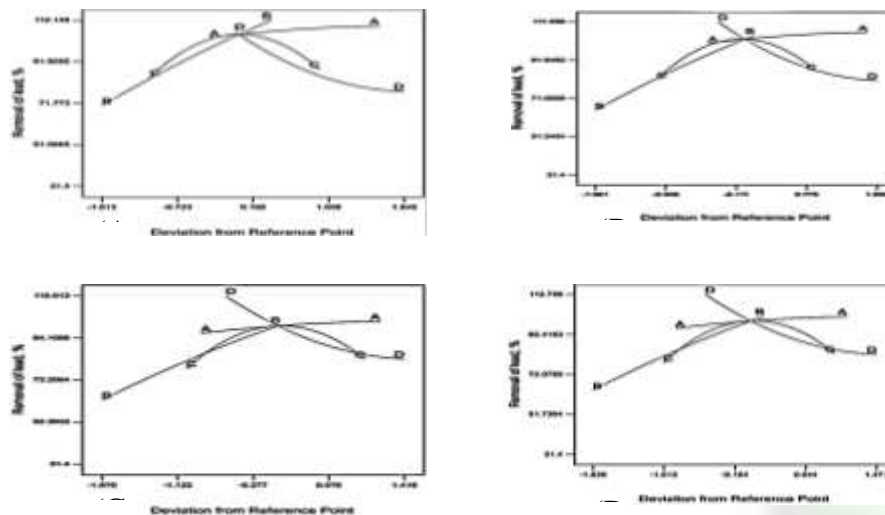


Fig. 10: The predicted optimum solutions for the uptake of lead, (A) predicted solution 1, (B) predicted solution 2, (C) predicted solution 3 and (D) predicted solution 4.

Conclusion

Porous graphitic carbon was synthesized from medium grade El Maghara Egyptian bituminous coal by thermal and chemical treatments. The applicability of the synthetic porous graphitic carbon as adsorbent of lead was tested according to the response surface methodology with Central Composite rotatable statistical design. Second order Polynomial model was selected to represent adsorption process, effect of the selected parameters, interaction between them and the predicted optimizing solutions. Based on the model F values and the good agreement between the actual and the predicted results, the second order polynomial model was significant and suitable to represent the relation between the selected parameters and the required responses (amount of Pb^{2+} adsorbed and removal of Pb^{2+} , %). The experimental runs revealed that the lead uptake was highly dependent on pH of the solution and the best removal efficiency occurred at pH from 4.5 to 5 by using 0.5 g of porous carbon and 50 mg/L lead concentration mass at 120 min contact time. Using the Design Expert's Optimization Function, optimum experimental results can be enhanced through a series of predicted optimum solutions from 1 to 4 as mentioned above.

Acknowledgments

The authors thank the support and project finance office, Beni-Suef University, Egypt for financially supporting this study.

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Cite this article as:

Essam A. Mohamed, Ahmed M. Zayed, Ali Q. Selim, Suzan S. Ibrahim, Moaaz K. Seliem-Response surface modeling and optimization of lead uptake from aqueous solution by porous graphitic carbon synthesized from Egyptian bituminous coal. *International Journal of Bioassays* 5.6 (2016): 4607-4616.

Source of support: Beni-Suef University, Egypt

Conflict of interest: None Declared