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Synthesis and Characterization of Zeolite Templated Carbon and Usage as Adsorbent for Removal of Pb(II) Ions from Solution

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Abstract: In this study, the porous carbon was prepared through templated synthesis method using the natural zeolite as template and sugar as carbon source. The porous carbon was obtained at a carbonization temperature of 700^{o}C with a weight ratio 1:1 for zeolite and sugar. The physical, structural and surface properties of the porous carbon were characterized with the scanning electron microscope (SEM), transmission electron microscope (TEM), X-ray diffraction (XRD), elemental analysis and nitrogen (N_2) adsorption. The specific surface area and total pore volume of carbon were found as 412 m^2/g and 0.5515 cm^3/g, respectively. This carbon material was used for removal of Pb^{2+} ions from solution. The effects of initial pH, temperature and contact time on adsorption were studied. The maximum Pb^{2+} removal was observed at pH=5. The adsorption was reached to the equilibrium in 120 minutes. Various kinetic models were used for describing the adsorption kinetic and the pseudo-second order kinetic model showed well fit. Langmuir, Freundlich and Temkin isotherm models were applied to the experimental equilibrium data and Langmuir equation was found as best fitting isotherm.

Keywords: Templated carbon, Characterization, Adsorption, Lead

Introduction

Waste and toxic heavy metals as a result of various industrial activities cause direct water pollution. Oil refinery wastes, paper, metal coatings, detergents, food, plastics, pharmaceuticals and industrial wastes and wastewater are important pollutants in terms of heavy metals. Heavy metal ions in industrial effluents can pose severe hazards to the human health, living resources and ecological systems due to their strong toxicity, environmental persistence and bioaccumulation (Ma et al., 2017). Lead is the one of the most hazardous heavy metal. According to the Institute for health metrics and evaluation, more than half million deaths per year are caused by the lead exposure which has prompted research into the removal lead from water (Sawant et al., 2017; Pawar et al., 2018). Therefore, the efficient removal of Pb(II) from wastewater is very important subject. In order to remove heavy metals, many methods have been used, which include chemical precipitation, ion exchange, membrane filtration, adsorption and ultrafiltration. Among these methods, adsorption is one of the most promising methods due to characteristics of cost-effective, high efficiency and easy operation (Tang et al., 2018; Ma et al., 2017).

Carbon materials are used in many applications such as adsorption, catalysis, water and air purification or energy storage. These materials are inert, offer high surface area and large pore volume and have high mechanical stability (Böhme et al., 2005). The hydrophobic nature of their surfaces is the most important feature for many applications (Santos et al., 2010). Activated carbons are the most commonly used carbonaceous materials. These materials are produced by various methods from carbonaceous raw materials. The pore structure of carbon material is one of the most important properties that determine its use in a specific process. Optimization of experimental parameters during the carbonization/activation steps allows the design of structural properties of carbons. Template synthesis has been proposed in the literature as a suitable method for obtaining porous carbons with well-defined structural, surface and chemical properties. This method mainly involves filling the pores of the template material with the carbon source (impregnation), carbonization and removal of the template material from the structure (Barata-Rodrigues et al., 2003).

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In this study, the porous carbon was produced with the templated synthesis by using natural zeolite as the template and sugar as the carbon precursor. The carbon synthesized was characterized by nitrogen adsorption, XRD, SEM, TEM, and elemental analysis. Pb(II) adsorption from aqueous solution on the porous carbon was examined and the effect of parameters such as pH, adsorption time and temperature on the adsorption were determined.

Method

Preparation of Porous Carbon

The natural zeolite obtained from Manisa region, Turkey was selected as the template material and was crushed, sieved and dried before the operation. The sugar was used as the carbon precursor.

The aqueous suspension containing 10 g of zeolite, 10 g of sugar and 100 mL of water was prepared with a weight ratio 1:1 for zeolite and sugar. Then, 1 mL of concentrated H_2SO_4 was added to the suspension and mixed in the magnetic stirrer for 24 hours. The mixture was kept at room temperature for 24 hours. Following, the samples were dried at 100°C for 24 hours, and then carbonized at 700°C under nitrogen flow. In the carbonization process, the samples were heated under nitrogen flow at a heating rate of 10°C/ min to 700°C, held at this temperature for 1 hour and cooled again under nitrogen flow. The resulting sample was treated with HF solution in order to obtain the carbon phase. Then carbon sample was filtered and washed with distilled water. Finally, the carbon sample was dried at 100°C for 24 hours.

Characterization of Porous Carbon

The surface area, pore volume and pore size distribution of porous carbon were determined by N_2 adsorption at 77 K with Quantachrome Autosorb 1C surface characterization device. The surface area was calculated from adsorption isotherm by using Brunauer-Emmett-Teller (BET) equation. The total pore volume was calculated at a relative pressure of 0.99. The micropore volume was determined by t-plot method. The pore size distribution was determined Density Functional Theory (DFT) method.

X-ray diffraction (XRD) analysis was performed by a Rigaku Rint 2200 diffractometer with Cu K radiation.

The surface morphology was investigated by a scanning electron microscopy (SEM) (Jeol, JSM5600LV) and a transmission electron microscopy (TEM) (FEI Tecnai G^2 Spirit Bio(TWIN)).

Elemental analysis of carbon sample was performed by a LECO, CHNS-932 elemental analyser.

Adsorption Studies

In the batch adsorption experiments, 50 mg of adsorbent and 25 mL of Pb(II) solution in the range of 10-60 mg/L were stirred at known temperatures (25-45^{o}C) for 3 hours. After adsorption, the concentration of Pb(II) was determined by using UV spectrophotometer. To study of the effect of the initial pH on the adsorption, the solution pH was adjusted in range of 2-6 by addition of HCl and NaOH. In this experiment, 50 mg/L of initial concentration and 25^{o}C of temperature was kept constant. In kinetic experiments, 250 mL of lead solution (50 mg/L) and 0.25 g of carbon were mixed and the concentration was measured at different time intervals.

The amount of adsorption capacity, q_e (mg·g^{-1}) was calculated according to following equation:

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

where C_0 and C_e are the Pb^{2+} concentrations in solution before and after adsorption (mg/L), respectively. V is the volume of solution (L), and m is the mass of the adsorbent (g).

Results and Discussion

Characterization Results of Porous Carbon

The N_2 adsorption-desorption isotherm of the porous carbon prepared by templated synthesis was given in Figure 1. It is seen that the isotherm is Type IV based on the classification of Brunauer, Deming, Deming and Teller (BDDT). Generally, this type of isotherms represents a solid with micro and mesoporous structure. According to the surface properties given in Table 1, the mesopore volume was higher than micropore volume about four times. The average pore diameter was 54 Å indicating that the carbon forms mainly mesopores. This situation can be shown from pore size distribution given in Figure 2. The templated porous carbon includes mostly mesopores around 20-60 Å as well as micropores around 7-20 Å.

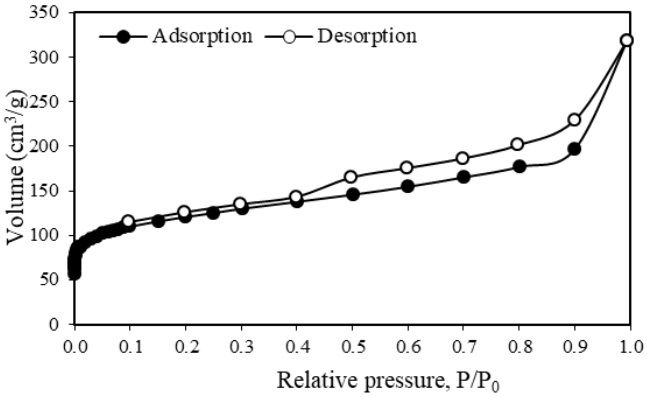


Figure 1. The N_2 adsorption-desorption isotherm of the porous carbon

Table 1. Surface properties of the porous carbon

S_{BET} (m^2/g)	V_T (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Dp (Å)
412	0.5515	0.1220	0.4295	54

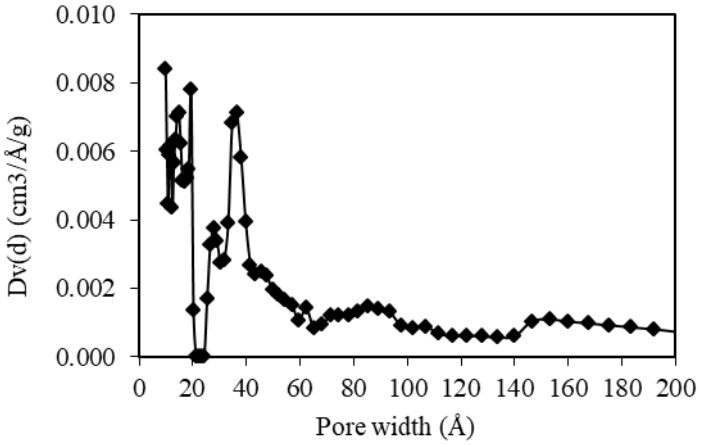
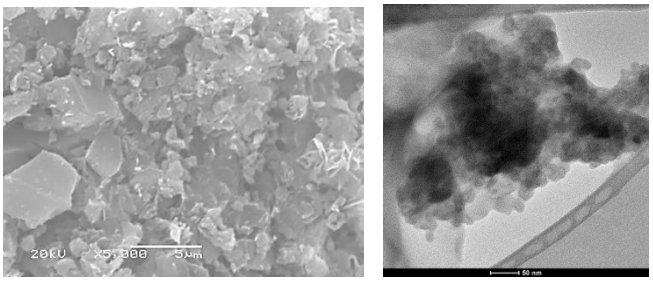


Figure 2. Pore size distribution of the porous carbon

SEM and TEM micrographs of the porous carbon were given in Figure 3. The porous carbon synthesized with zeolite template shows cavities on their external surface that improve the porosity. Different pore size and shapes were observed on the surface.



(a) **(b)**

Figure 3. (a) SEM and (b) TEM micrographs of the porous carbon

The XRD spectrum of the synthesized carbon sample was given in Figure 4. The broad peak in the 2 region of 20-30°is the characteristic peak of a disordered carbonaceous structure which is corresponding to the 002 reflection from the parallel stacking of graphenes and with interlayer spacing of 3.06 A^{o}. The broad 002 peak can be ascribed to stacking of graphenes of small dimensions in a parallel fashion (Bakandritsos et al., 2004; Sakintuna and Yürüm, 2006).

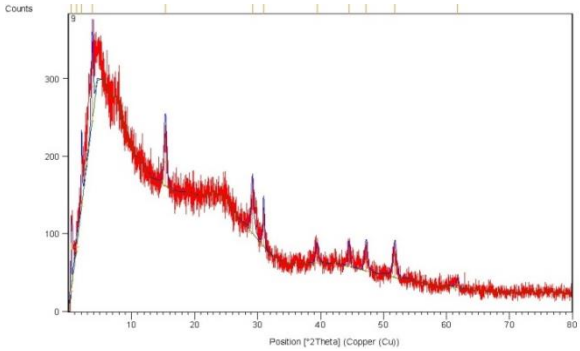


Figure 4. The XRD spectrum of the porous carbon

According to the elemental analysis results, the carbon content of the zeolite templated carbon is observed as 60.2%. This value may indicate that the zeolite template was not successfully removed at the demineralization step.

Results of Adsorption Studies

Effect of Initial pH

The effect of the initial pH on adsorption of Pb^{2+} on the zeolite templated carbon was shown in Figure 5. It can be observed that the removal of Pb^{2+} increased with increasing pH from 2 to 5. The maximum adsorption was found as 7.11 mg/g at pH 5. The adsorption decreased when the pH was increased to 6. At low pH values, adsorption is very weak due to the competition between bivalent metal ions and H^{+} ions. The increase in the lead removal with the increasing pH can be explained on the basis of a decrease in competition between H^{+} ions and metal species for the surface functional group (Barczak et al., 2015).

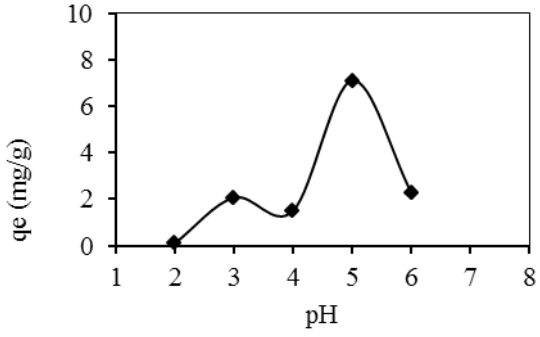


Figure 5. Effect of initial pH on the adsorption of Pb^{2+}

Adsorption Kinetics

The effect of the time on the adsorption uptake is shown in Figure 6. It can be seen that the adsorption of Pb^{2+} on the zeolite templated carbon reached to the equilibrium state in 120 minutes. No appreciable change in the adsorption is observed beyond this time.

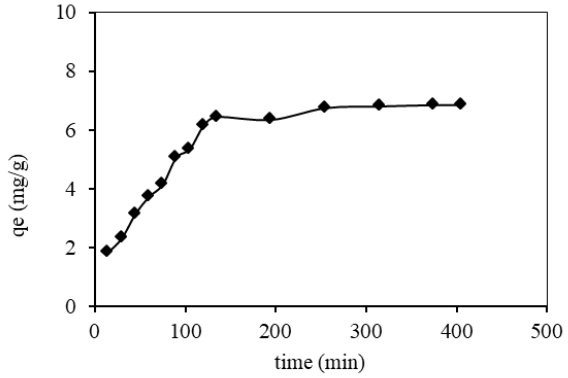


Figure 6. Effect of time on the adsorption of Pb^{2+}

The rate constants of the adsorption of Pb^{2+} on the zeolite templated carbon were determined using the pseudo-first order and the pseudo-second order kinetic models. The pseudo-first order and the pseudo-second order kinetic rate equations are given following equations, respectively:

$$ln(q_e - q_t) = lnq_e - k_1 t \quad (2)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

where q_e and q_t are the amount of adsorption (mg/g) at equilibrium and at time t, respectively; k_1 is the rate constant of pseudo-first order adsorption (min^{-1}) and k_2 is the rate constant of pseudo-second order adsorption (g/mg min). The values of k_1, k_2 and q_e can be calculated from the plots of $ln(q_e-q)$ against t for pseudo-first order and t/q_t against t for pseudo-second. As it can be seen from Table 2, the pseudo-second order equation describes better the adsorption kinetics. The pseudo-second order kinetic model assumes that the rate limiting step may be chemisorption involving valence forces due to the sharing or exchange of electrons between metal ions and adsorbent (Barczak et al., 2015).

Table 2. Kinetic parameters for the adsorption of Pb^{2+} onto the porous carbon

Model	Parameters	
Pseudo-first order	q_e (mg/g)	4.614
	k_1 (min^{-1})	0.0047
	R^2	0.8120
Pseudo-second order	q_e (mg/g)	8.012
	k_2 (mg/g min)	0.0022
	R^2	0.9905

Adsorption Isotherms

Adsorption isotherm studies were carried out at 25, 35 and 45°C temperatures. The adsorption isotherm data were analyzed according to Langmuir (Eq.4), Freundlich (Eq.5) and Temkin (Eq.6) models.

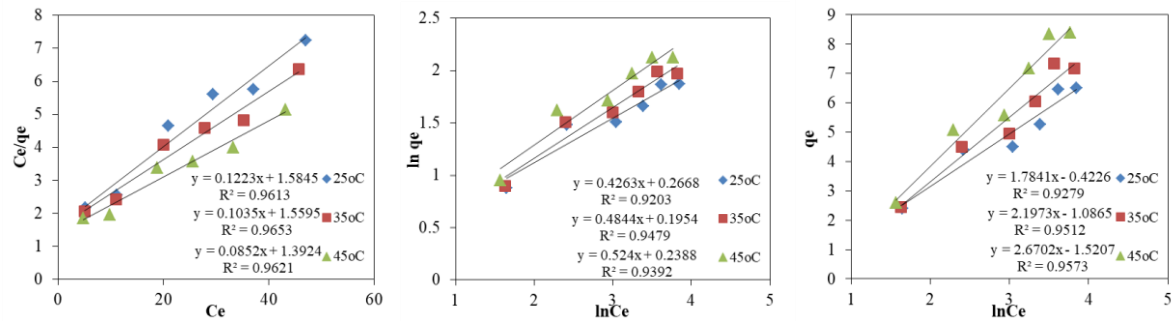
Langmuir equation: $$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \quad (4)$$

Freundlich equation: $$lnq_e = lnk_f + \frac{1}{n} ln C_e \quad (5)$$

Temkin equation: $$q_e = B_1 lnA + B_1 lnC_e \quad (6)$$

The isotherm plots are shown in Figure 7 and the corresponding parameters are given in Table 3. According to R^2 values, the Langmuir equation fitted well with the experimental data than the other isotherms. The Langmuir

monolayer adsorption capacity (q_m) increased from 8.17 to 11.73 mg/g as the temperature increased from 25°C to 45°C, indicating that the adsorption of Pb^{2+} on the porous carbon is an endothermic process.



(a) (b) (c)

Figure 7. Langmuir plot (a), Freundlich plot (b) and Temkin plot(c) for the adsorption of Pb^{2+}

Table 3. Adsorption isotherm parameters for the adsorption of Pb^{2+} onto the porous carbon at various temperatures

Model	Parameters	25°C	35°C	45°C
Langmuir	q_m (mg/g)	8.17	9.66	11.73
	b (L/mg)	0.0772	0.0664	0.06112
	R^2	0.9613	0.9653	0.9621
Freundlich	k_f	1.3058	1.2158	1.2697
	n	2.3457	2.0646	7.1397
	R^2	0.9203	0.9479	0.9392
Temkin	A	0.7891	0.6099	0.5658
	B_1	1.7841	2.1973	2.6702
	R^2	0.9279	0.9512	0.9573

Conclusion

In this study, porous carbon was obtained via templated synthesis method by using natural zeolite as a template and sugar as a carbon source. The porous carbon was characterized by several techniques such as N_2 adsorption, SEM, TEM, XRD and elemental analysis. The specific surface area and total pore volume of the zeolite templated carbon were found as 412 m^2/g and 0.5515 cm^3/g, respectively. The pore structure of carbon is mainly composed of mesopores.

The adsorptive removal of Pb(II) from aqueous solution was carried out using synthesized templated carbon. It was shown that the pseudo-second order kinetic model provided the better correlation for the adsorption data. The equilibrium sorption data were analyzed using Langmuir, Freundlich and Temkin models. The results fitted well to the Langmuir model. It was obtained maximum sorption capacities as 8.17 mg/g, 9.66 mg/g and 11.73 mg/g at 25, 35 and 45°C temperatures, respectively. According to the results obtained, it can be said that this templated carbon can be used as an adsorbent for Pb (II).

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