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Recycling of Rose Wastes to Activated Carbon with Ecological Precursor

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Abstract: Nowadays environmental damage of heavy metals is increasing and that becomes a big problem for human and human health. Especially after the industrial revolution, increasing of production and consumption materials, adversely affect the environment. Among all the pollutions, heavy metal is an important part. Because they are toxic or poisonous even at low concentration. The most widely used process is activated carbon adsorption for heavy metal adsorption from wastewater. Activated carbon can produce from carbon containing substances. Turkey is an important rose oil producer of the world and every year over 12 000 tons of rose processing wastes produced. In this study, activated carbon was obtained from rose crops of rose oil factories. There are some activation methods for increasing surface area of the carbon. In this study, potassium chlorate ($KClO_3$) was used for increasing carbons surface area. $KClO_3$ never used before for activation. The thermal decomposition of $KClO_3$ (potassium chlorate) generates KCl and O_2 gas. Effects of O_2 gas outlet on the pore size of activated carbon were studied. The surface characterization was examined with Brunauer-Emmett-Teller (BET) analysis and Pb^{+2} adsorption capacity of obtaining activated carbon was determined by inductively coupled plasma optical emission spectrometry (ICP OES) analysis.

Keywords: Activated carbon, rose waste, $KClO_3$ activation, waste utilization, Pb^{+2}, adsorption

1. Introduction

Environmental issues are at the beginning of the most important hazards that threaten human and animal health and these problems are growing every passing day. The limit of waste elimination capacity and durability of nature is known to be very high within their functions, but the human-induced factors force the limit of the capacity to withstand, even exceed. On this purpose, human beings have used the methods of waste treatment in order to help nature which are still artificial. Most of the waste treatment methods and systems used for waste elimination are very effective. However the problems caused by the disposal of secondary wastes occurred during the process as a consequence are on the other side of the coin. Thus the scientists are working to develop new environment-friendly treatment systems. It should be provided to contribute in both environment and economy via the use of organic and inorganic substances, especially in nature and the environment, or the waste products and surplus resulting from the human activities (industry, agriculture, domestic, etc.).

Lead has the feature of being the most first important harmful metal to human activities and the eco-system. Lead is the most important heavy metal which bears environmental pollutants because it is toxic in any case and it is propagated as a metal or a compound in the atmosphere. Lead causes people with acute and chronic effects on people. Especially it harms the liver and stomach of people in a short period of time and it harms the brain and kidneys in a long time. Some of the heavy metals are required for humans and animals as a nutrient. Therefore, many countries have set standards for drinking water and they have developed regulations in regard to the discharge of industrial wastewater for not polluting the drinking water resources (Karaboyacı, 2010). One of the most effective methods for heavy metal treatment is to filter the wastewater with activated carbon. Therefore the production of cheaper activated carbon and consequently the wastewater purification becomes more important. Therefore, in recent years, many studies have examined the preparation of activated carbon from low-cost and readily available materials, mainly industrial and agricultural byproducts.

The formation of porosity which is the most important feature of activated carbon, is provided via the activation process that is followed by carbonization (Bandosz, 1999; Gergova and Eser, 1996). In the activation process, the volume and the radius of the pores that are formed in the carbonization process increase and new pores are developed. The conditions of carbonization and the structure of the raw material determine the pore structure and the pore size distribution. In order to obtain activated carbons which are porous and have a high surface area there are two types of activation methods: physical activation and chemical activation.

Agricultural wastes are lignocellulosic materials containing three basic structural components as hemicellulose, cellulose and lignin. Besides these they also contain some extractive components. In general, these three components have a relatively high molecular mass that highly participates in the total mass. However the extractives have a very low contribution to the main mass because of their low molecular structures. Lignocellulosic structures are also referred as "photo mass" as they are formed as a result of photosynthesis (Giraldo and Moreno-Piraján, 2008). For this purpose, highly porous and capable activated carbons can be produced via a wide range of different agricultural waste products such as tree bark, apricots, almonds, cherries and olives, beans, nuts, peanuts, and walnuts.

The average amount of the rose flower produced in Isparta is over 12 000 tons / year between 1986 and 1999. However in recent years, there has been a steady reduction and this amount has decreased to the level of 6000 tons/year. Rose pulp has occurred 27 000 tons per year between 1986 and 1999 in Isparta (wet weight). Rose pulps that have occurred during rose processing season lasting about 45 days, are filled in the earth pits opened around the facility or discharged into the stream beds. This situation also causes odor and visual pollution besides the water pollution around the plants built by the wayside (Tosun et al., 2003).

In this study, the conversion of rose pulp to activated carbon, which has no area of use today and the possibilities of improving the performance of this product by activating via various chemicals are investigated. $KClO_3$ was used as chemical activation agent.

2. Materials and Methods

2.1. Rose pulp

The rose pulp used in this study is obtained from the rose oil plants in Isparta. Rose pulps are dried at room temperature before being used in the study. After the drying process, the rose pulps are minimized to the desired particle diameter by grinding robot after the drying process. Rose pulp has been sifted through the sieves with 300 and 180 micron mesh respectively and the remaining material between two sieves has been used for homogenous particle size.

2.2. Chemicals and measurements

All the chemicals used in the study are in analytical purity. As a stock 1000 mg/L Pb (II) solution is prepared by using Lead(II) nitrate ($Pb(NO_3)_2$) The Pb (II) solution which used in adsorption experiments was prepared by being diluted from this stock solution. For arranging the pH, 0.1 M NaOH and 0.1 M HCl solution were used. For determining the activated carbons heavy metal adsorption capacity, the filtrates were analyzed with ICP-OES device. 3% and 5% $KClO_3$ by weight of rose pulp were used in chemical activation process.

2.3. Chemical activation

3% and 5% $KClO_3$ by weight of rose pulp was used for chemical activation. $KClO_3$ was solved in 10 mL of water and 10 grams of rose pulp added to the solution. The mixture was mixed in to provide absorption of all $KClO_3$ solution by rose pulp. Rose pulp was dried at room temperature and after drying it was converted to activated carbon by pyrolysis.

2.4. Thermal activation

Rose pulp has been converted into activated carbon by pyrolysis at 1000 °C. Rose pulp was put in a ceramic boat and pyrolysis in a tube oven under nitrogen gas. Rose pulp was pyrolyzed for 60 minutes. Obtained activated carbon samples, have been washed with distilled water to remove from the on-site residues and allowed to dry at room temperature.

2.5. Determining the optimum pH value

In order to determine the effect of pH value on the adsorption capacity, adsorption tests at different pH values have been performed. pH interval for Pb (II) adsorption experiments are selected as 2-7. 50 mg adsorbent (1 g/L) has been added to 100 ppm 50 mL Pb^{2+} solution and shaken for 1 hour in an orbital incubator at 100 rpm and 25 °C. The mixture has been shaken within the orbital incubator at 100 rpm and 25 °C for 1 hour. In order to observe whether there is any precipitation in terms of metal ions during the absorption process, the control samples with a pH value adjusted at the requested value that don't consist of any activated carbon, are shaken with the other mixtures at the same time. After the shaking process, the activated carbon is filtered from the solution and the metal concentration in the filtrate is determined by ICP OES analysis. The pH value obtained by the maximum adsorption capacity is accepted as the optimum pH value.

2.6. Kinetic studies

In order to determine the equilibrium time of adsorption, 50 mL Pb^{2+} solution with 100 mg/L concentration is placed in vials at optimum pH values. The mixtures prepared by adding 50 mg (1g/L) adsorbent in the vials was stirred in an orbital incubator at 100 rpm and 20 °C for 1, 3, 5, 15 and 30 minutes. At the end of the period, the adsorbent is filtered by using a 1 µm pore sized filter paper. Metal concentrations in the filtrates are measured by ICP OES.

2.7. Isotherm studies

In order to determine the equilibrium status of the absorbance process of activated carbon for heavy metals, isotherm experiments are performed. It represents the amount of metal bound on the adsorbent surface as a function of the material present in the solution. For this purpose, activated carbon with 25, 50, 75, 100, 125 and 150 mg (0.5, 1, 1.5, 2, 2.5, 3 g/L) dry weights have added to the solution containing 50 ml 100 mg/L $Pb2^{+}$ and the mixture is shaken in an orbital incubator at 20, 30 and 50 °C temperature until the equilibrium period specified by the kinetic studies. Then, mixes were filtered and their Pb^{+2} concentrations were determined by ICP OES. The experimental data obtained is analyzed according to the nonlinear regression analysis and Freundlich and Langmuir isotherm parameters are calculated.

3. Result and Discussion

3.1. Optimum pH values

Graldo and Pirajá (David and Hon, 1995) have reported in their study performed for Pb^{2+} adsorption with activated carbon obtained from lignocellulosics that the type in the solution that is dominant up to pH 6 is water-soluble Pb^{2+} , approximately 6 water-soluble forms of $Pb(OH)_2$ and $Pb(OH)^+$ and $Pb(OH)_2$ starts to precipitate after pH.

Lead species found between pH 2 and 8 are Pb^{2+}, $Pb(OH)_{2(S)}$ and $Pb(OH)^+$, which may interact with the solid surface due to its textural and electrostatic characteristics, with these latter affected by the surface chemical groups and the pH of the solution. Therefore optimum pH studies are performed between pH 1-6 and the results given in Figure 1 are obtained. As it can be clearly seen from figure 1, optimum pH values for all adsorbents are about 5.5. In the previous studies it is indicated that the adsorbent surface at low pH values can be positively loaded with H^+ ions. In our study, data is obtained that is corroborative with these results.

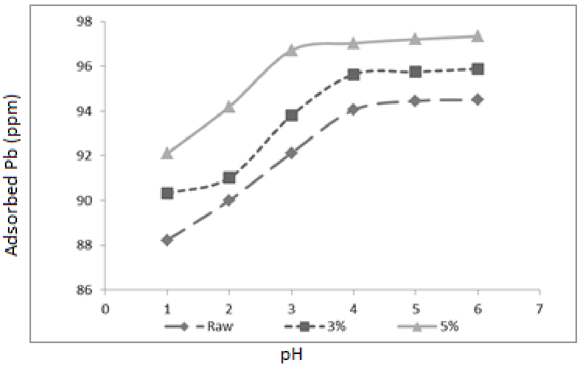

Figure 1. Optimum pH values of activated carbons

3.2. Results of the kinetic studies

Kinetic studies are performed in order to determine the capture rate of the pollutant in the solution by activated carbon. Thus Figure 2 shows the pseudo 1st and 2nd kinetic graphics that is drawn as a result of the experiment performed for the activated carbon obtained from the raw rose pulp. In this equations; qe represents the amount of metal ion adsorbed during the equilibrium time (mg/g), K_1 represents the pseudo first order kinetic constant (min^{-1}), K_2 represents the equilibrium rate constant of pseudo-second order sorption ($g.mg^{-1}\ min^{-1}$) and R^2 is the correlation coefficient.

When 1st and 2nd order pseudo kinetics graphics of the raw rose pulp have been analyzed, it is seen that approximately 69% of the adsorption process has been completed in the first 5 minutes. This is an indication of that the adsorption process occurs quickly. It is observed that the adsorption process is completed after 15 minutes. It is seen from the chart, experimental data are compatible with the same rate in both kinetic models.

Figure 3 shows the 1st and 2nd order pseudo kinetics graphics of the activated carbon obtained from rose pulp which is treated with 3% $KClO_3$. When the graphic is analyzed, it is observed that approximately 75% of the adsorption process has been completed in the first 5 minutes and the adsorption process is completed after 15 minutes. In the experimental studies, it is observed that adsorption process has been completed in the first 5 minutes. It looks like experimental data are compatible with the same rate in both kinetic models. So the adsorption process for this activated carbon occurs more quickly.

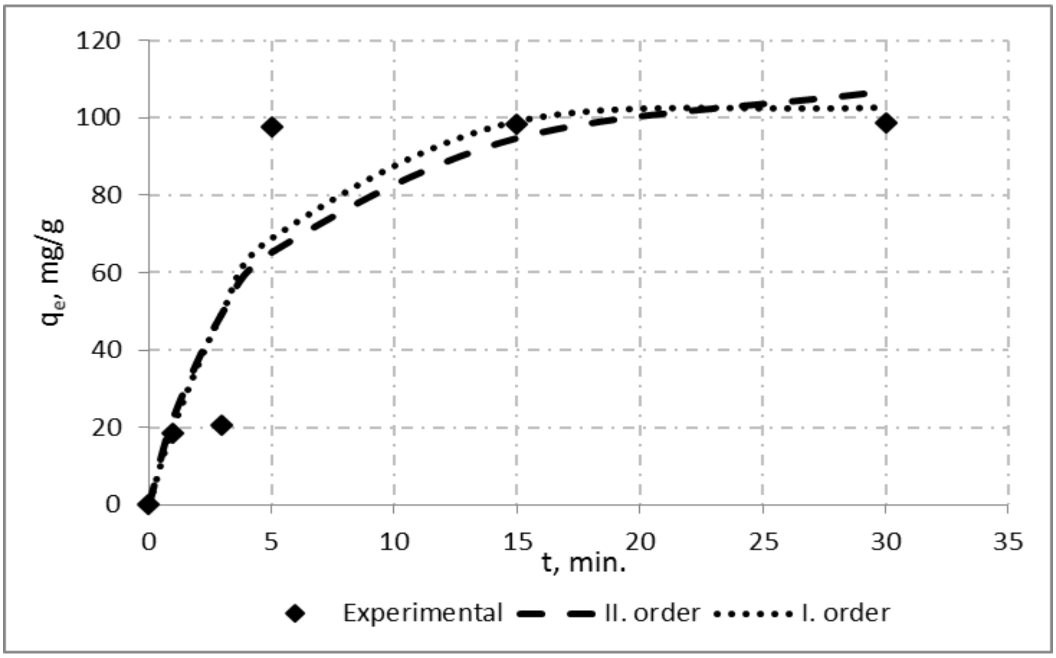

Figure 2. The pseudo 1. and 2. order kinetical graphics of the adsorption process for raw activated carbon

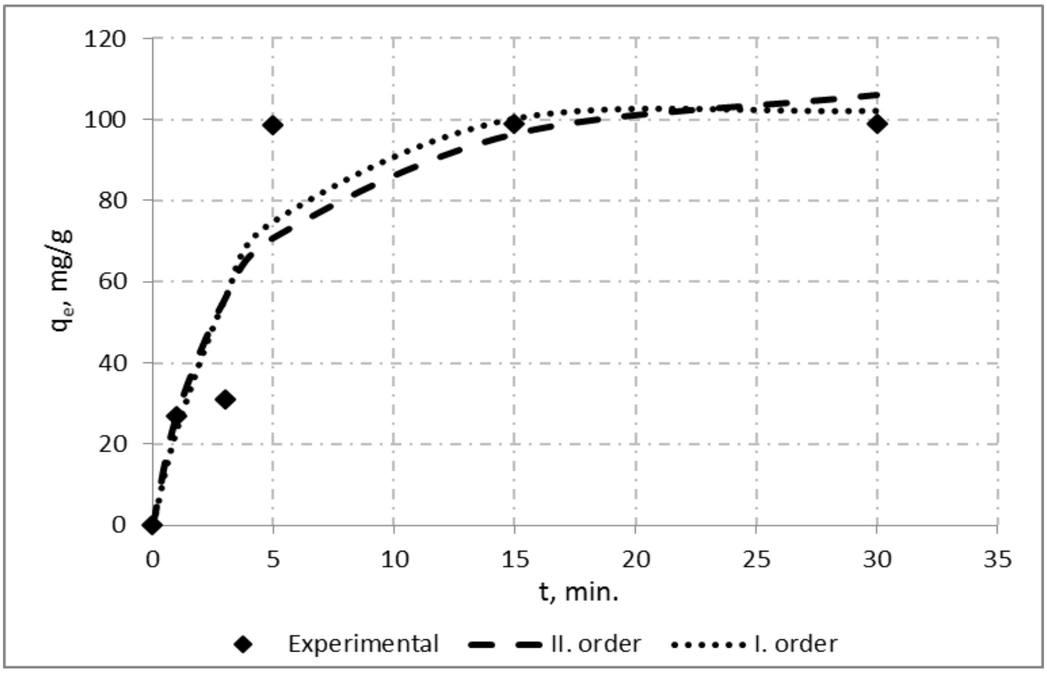

Figure 3. The pseudo 1. and 2. order kinetical graphics of the adsorption process for activated carbon treated with 3% $KClO_3$

Figure 4 shows the 1st and 2nd order pseudo kinetics graphics drawn for the activated carbon that is obtained from the rose pulp treated with 5% KClO3. When the graphic is analyzed, it is observed that 76.2% of the adsorption process is completed in the first 5 minutes and the process is completed at the end of 15 minutes. In experimental studies, it is observed that adsorption is completed in the first 5 minutes. So calculations are compatible with experimental data and process occurs so quickly.

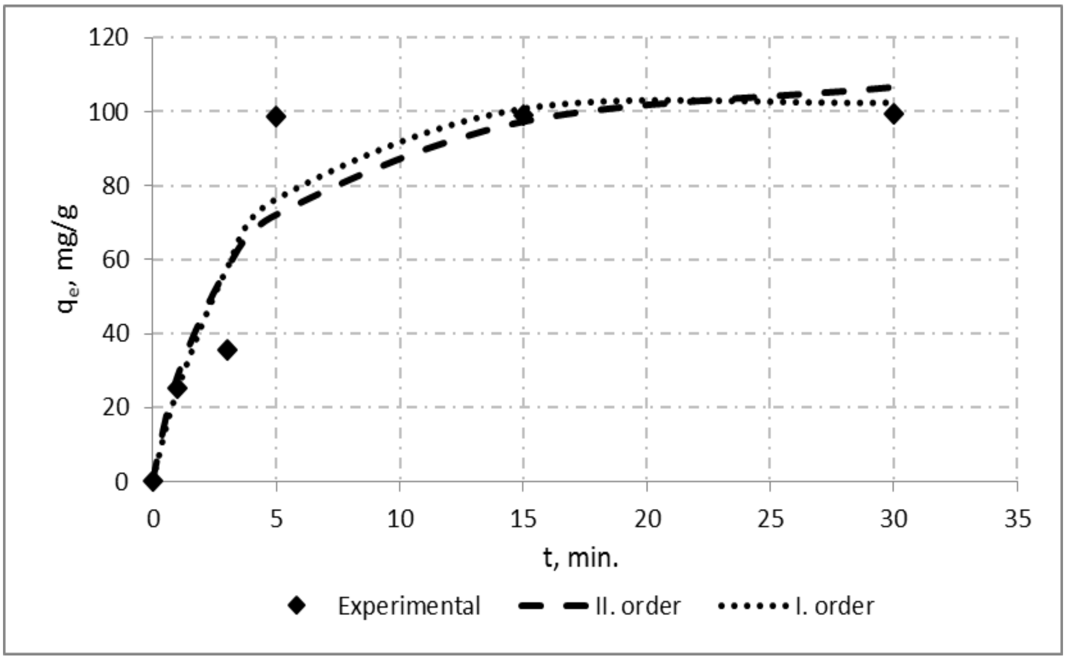

Figure 4. The pseudo 1. and 2. order kinetical graphics of the adsorption process for activated carbon treated with 5% $KClO_3$

It can be seen that the R^2 values in Table 1 comply with 1st order pseudo kinetic model of adsorption process better in all three activated carbons. However the values obtained for both models are very close to each other. It can be assumed that the two reactions can be present of which the first one reaches equilibrium quickly and rapidly and the latter may last for a long and slow period of time. These two reactions may occur in series or parallel in the adsorption process (Khambhaty et al., 2009). A good concordance of the experimental data with pseudo I and II models indicate that both physical and chemical adsorption effects process in Pb^{2+} adsorption acts at the same time. When the adsorption capacities in table 1 were analyzed, results show that the 1st order kinetic model has approximately 102 mg/L specific adsorption capacity for all three adsorbents and this data matches to the experimental data and at this point we can think that adsorption has a dominant effect on adsorption process.

	$K_{1.ad}$	q_e	R_1^2	q_e	$K_{2.ad}$	R^2
Raw	0.221	102.78	0.849	122.57	0.0018	0.822
3% $KClO_3$	0.264	102.15	0.880	117.83	0.0025	0.855
5% $KClO_3$	0.273	102.38	0.902	117.76	0.0026	0.876

Table 1. Pseudo 1. and 2. order kinetic model constants and regression numbers of the activated carbons.

3.3. Results of the isotherm studies

Adsorbing process continues until a balance is formed between the material concentration accumulated on the adsorbent and the material concentration remained in the solution. Mathematically this balance is explained by the adsorption isotherms. Figure 5 shows the Langmuir and Freundlich Isotherm graphics of Pb(II) adsorption of activated obtained from the raw rose pulp. In this table K_F represents the proportional adsorption capacity, a parameter that belongs to the isotherm, n represents the adsorption density, qm represents the maximum monolayer adsorption capacity (mg/g), a^L represents the isotherm fix which states the adsorption energy (L/mg).

As in the kinetic studies, the results in the isotherm studies are also very close each other. When we consider the R^2 values, we see that this value is 0.9883 for Langmuir and 0.9655 for Freundlich.

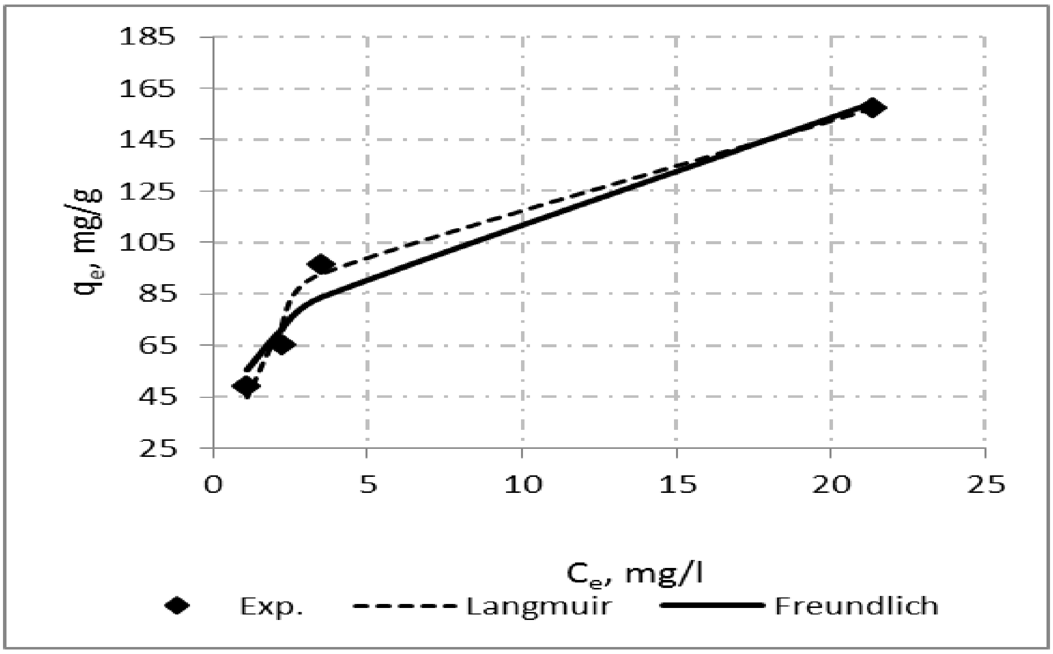

Figure 5. Raw activated carbon Pb(II) Adsorption's Langmuir and Freundlich Isotherm

Because these two values are very close to each other, we can argue that adsorbent of adsorption has an heterogeneous surface but Pb^{2+} forms a single layer saturated fixed plate on this heterogeneous surface.

In Figure 6, Langmuir and Freundlich isotherm graphics of Pb^{+2} adsorption of activated carbon obtained from rose pulp treated with 3% $KClO_3$ are seen. As seen from the graphics, values are very close to each other. When we observe the R^2 values, this value is 0.9586 for Langmuir and 0.9032 for Freundlich isotherm model. In this way, we can see that concordance to the Langmuir isotherm has increased when compared to the activatedcarbon obtained from the raw rose pulp. Thus we may conclude that treatment with 3% $KClO_3$ has made the surface more uniform.

Figure 7 shows the Langmuir and Freundlich isotherm graphics of the Pb^{+2} adsorption of activated carbon obtained from the rose pulp treated with 5% $KClO_3$. As can be seen from the graphics, experimental data here is closer to Langmuir isotherm. When we consider the R^2 values in table 2, we can see that this value is 0.9959 for Langmuir and 0.9452 for Freundlich. Considering this data, the increasing quantity of $KClO_3$ has reduced the heterogeneity of the surface. Namely, ionic points that may interact with metal cation on the surface can become homogeneous with by chemical activation.

The empirical form of Freundlich equation is applicable to monolayer adsorption (chemisorption) and multilayer adsorption (Van der Waals adsorption) Some authors explains that Langmuir isotherm corresponds to a dominant ion-exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the adsorption process (Fiol et al., 2006).

Table 2. Langmuir and Freundlich Constants of adsorbents

	Freundlich			Langmuir		
	n	K_F	R^2	a_L	q_m	R^2
Raw	0.3555	53.6432	0.9655	0.2986	182.08	0.9883
3% $KClO_3$	0.3042	58.3972	0.9032	0.3904	169.50	0.9586
5% $KClO_3$	0.3082	60.3921	0.9452	0.4298	172.23	0.9959

Since Langmuir and Freundlich adsorption models mathematically characterize the adsorption of diluted solutions, adsorption data in average dilution intervals show compliance for both isotherms. Due to the content in active binding centers at various centers in the heterogeneous surfaces, Freundlich model is a more realistic approach than the Langmuir model (Seydioğlu, 2009).

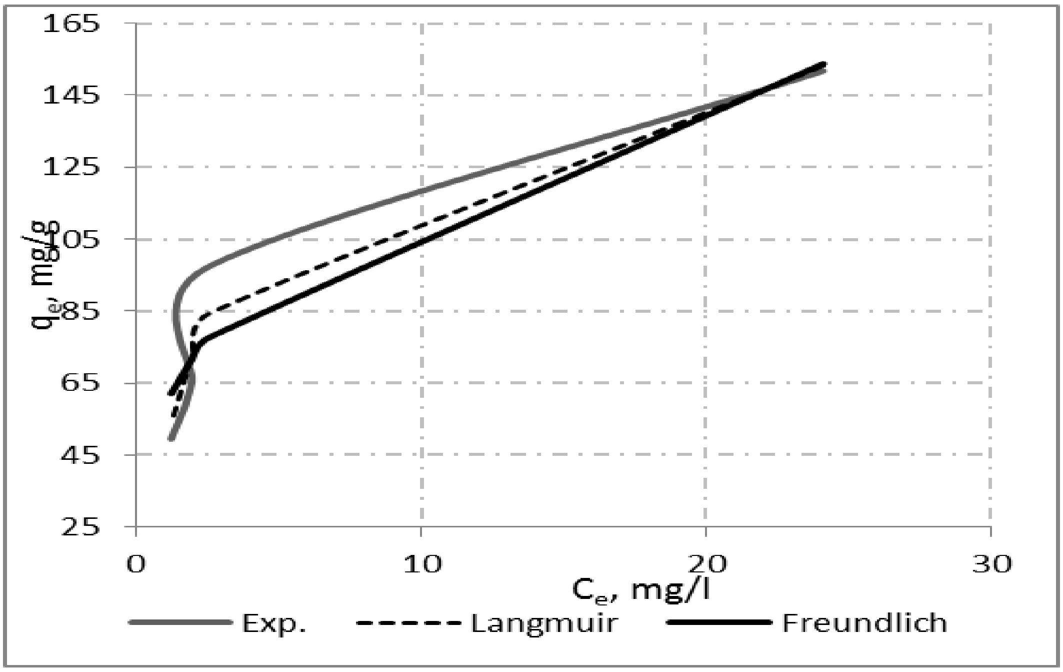

Figure 6. 3% $KClO_3$ treated activated carbon Pb(II) Adsorption's Langmuir and Freundlich Isotherm

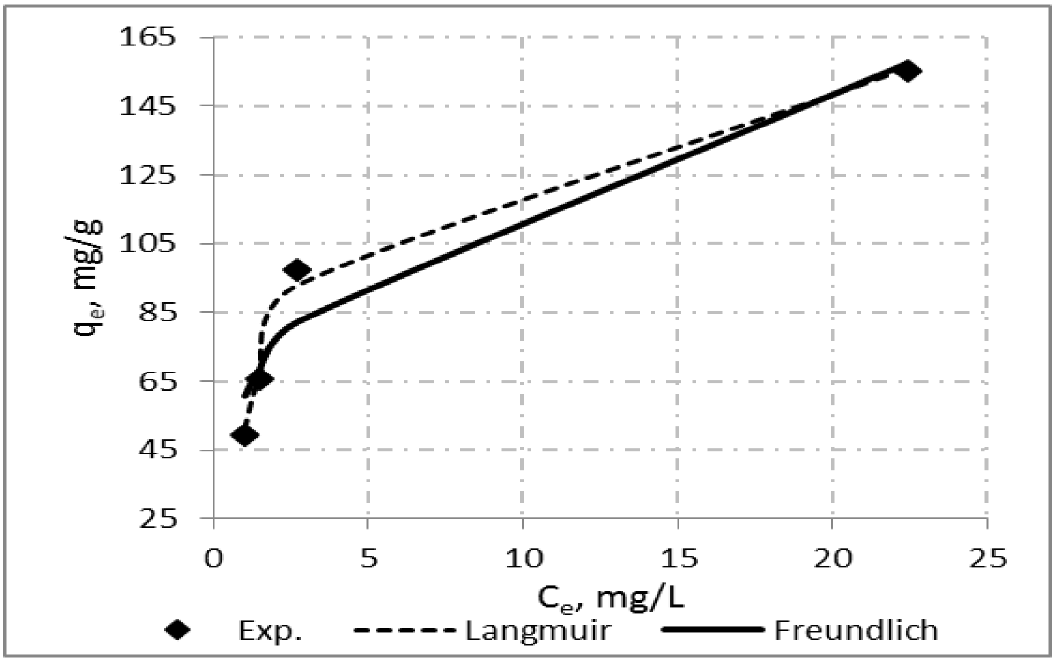

Figure 7. 5% $KClO_3$ treated activated carbon Pb(II) Adsorption's Langmuir and Freundlich Isotherm

In Table 3, the effect of the $KClO_3$ activation on the surface area is shown. $KClO_3$ releases oxygen gas by undergoing thermal decomposition at high temperatures. At this point our main expectation is that potassium chlorate, which has been absorbed by the rose pulp, generates O_2 gas by thermal decomposition and thus the outgoing O_2 gas creates new recesses and protrusions in the adsorbent and also on its surface. As expected, it had caused an increase of 1636% on the surface area of activated carbon that has been obtained from the rose pulp via $KClO_3$ treatment. The increasing chemical quantity has no effect on the increase in the surface area. Therefore, concentrations below %3 can be tried for more economical and ecological activation.

$$2\ KClO_3 \rightarrow 2\ KCl(s) + 3\ O_2\ (g) \qquad (1)$$

Table 3. BET surface area of three different activated carbons

BET Surface Area		
Raw	7.9943	m²/g
3% $KClO_3$	129.4916	m²/g
5% $KClO_3$	130.7575	m²/g

4. Conclusion

As a result, we can say that converting rose wastes to activated carbon is a good way to obtain cheaper activated carbon. Because today rose pulp is nothing more than waste. And also it is a good way for elimination and evaluation of rose wastes. $KClO_3$ is a good chemical activator that can increase the surface area 1636%. $KClO_3$ activation may be tried in commercial production of activated carbon. The Langmuir and Freundlich adsorption models were used to describe the equilibrium isotherm and isotherm constant calculation. It was found that the maximum equilibrium adsorption capacities were 182.08 mg/g, 169.50 mg/g and 172.23 mg/g for raw, 3% $KClO_3$ and 5% $KClO_3$ respectively.

Our study shows that activated carbon, which obtained from rose pulp is a good adsorbent for poisonous Pb^{+2} ions. Because it has a relatively high adsorption capacity compared to other studies in the literature. It can adsorb ions from solution both chemical and physical ways. Therefore, can say that the main interactions responsible from adsorption are weak chemical interactions such as Van der Waals interactions.

References

Bandosz, T.J. (1999). Effect of pore structure and surface chemistry of virgin activated carbons on removal of hydrogen sulfid, carbon, 37:483–491 doi:10.1016/S0008-6223(98)00217-6.

David, N.S., Hon (Ed.). (1995). Chemical modification of lignocellulosic materials. CRC Press, New York.

Fiol, N., Villaescusa, I., Martínez, M., Miralles, N., Poch, J., Serarols, J. (2006). Sorption of Pb (II), Ni (II), Cu (II) and Cd (II) from aqueous solution by olive stone waste. Separation and purification technology, 50(1), 132-140. doi:10.1016/j.seppur.2005.11.016.

Gergova, K., Eser, S. (1996). Effects of activation method the pore structure of activated carbons from apricot stone, carbon. 34: 879–888 doi:10.1016/0008-6223(96)00028-0.

Giraldo, L., Moreno-Piraján, J.C. (2008). Pb2+ adsorption from aqueous solutions on activated carbons obtained from lignocellulosic residues. Brazilian Journal of Chemical Engineering, 25(1), 143-151. Doi10.1590/S0104-66322008000100015.

Karaboyacı, M. (2010). Modifiye edilmiş lignoselülozikler ile ağır metal adsorpsiyonu. Süleyman Demirel Üniversitesi, Fen Bilimleri Enstitüsü, Doktora Tezi, Isparta. s113.

Khambhaty, Y., Mody, K., Basha, S., Jha, B. (2009). Kinetics, equilibrium and thermodynamic studies on biosorption of hexavalent chromium by dead fungal biomass of marine Aspergillus niger. Chemical Engineering Journal, 145, 489-49 doi:10.1016/j.cej.2008.05.002.

Seydioğlu, G. (2009). Bitkisel Atıkların Granül Aktif Karbon Üretiminde Değerlendirilmesi. Anadolu Üniversitesi Fen Bilimleri Enstitüsü Çevre Müh. ABD Yüksek Lisans Tezi, Eskişehir.

Tosun, İ., Gönüllü, M.T., Günay, A. (2003). Gül posasının kompostlaştırılmasına gözenek malzemesi ve aşının etkisi. Yıldız Teknik Üniversitesi Dergisi., 2003/2 pp 93-102.