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PREPARATION OF ACTIVATED CARBON FROM SUNFLOWER SEEDS

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Abstract

Activated Carbon (AC) was prepared from sunflower seeds as cellulosic waste and then used for adsorption of Phosphate (KH_2PO_4) dissolved in water. Characteristics of prepared AC and adsorption properties were investigated. Chemical activation process was selected to prepare the activated carbon. The raw material was washed and dried in 100ºC for one hour. Then the procures were impregnated with H_3PO_4 as chemical agent in ratio of 1:3 (Weight of Material: Chemical Agent) for 3 days. Then, the obtained mixture was filtered and dried at 80ºC for one hour and burned at 600 for 3 hours. The obtained surface was 496 m^2/g. The adsorption of Phosphate was done at room temperature with the best result obtained in initial concertation of 3ppm. Also, the dose of activated carbon was 0.5g and the agitation speed of 200rpm for 90 minutes. The adsorption percentage was 90.278%. Surface analysis of activated carbon was done by Scanning electron microscopy (SEM), however in order to identify the appearance and disappearance of functional groups during different activation temperatures FTIR analyses was used.

***Keywords*:** Activated Carbon, Adsorption, Environment, Pollution.

Introduction

Activated Carbon is an amorphous solid with high specific of high porosity. It is a composition of aromatic configurations of carbon atoms linked by cross linking bonds. Activated carbon and graphite are two different forms of carbon where activated carbon has group of atoms stacked in disorganized shape and the disorganization level is based on the raw material used in preparing the activated carbon. AC is considered as one of the most important adsorbents. Carbon compose 87-97 % of the AC while the remaining consists of hydrogen, oxygen, nitrogen, sulfur, ash and soil alkaline silicate. The production of AC is a process of two steps: Carbonization and Activation, in the first step raw carbonaceous material is subjected in an inert atmosphere, then in the second step the carbonized carbon is activated using an activation agent. The purpose of the activation is to enlarge pore diameters and derive new pores Jankowska *et al.* (1991), and Keltsev (1980). It can be carried out in two forms physical or chemical. In the physical activation process, the carbonized raw materials are activated through high steam or CO_2 temperature with a range of 800-1100 ºC. Whereas, in the chemical activation process the carbonized raw material is subjected in chemical agents such as acid based (H_3PO_4, HCl, etc.), strong base (KOH, NaOH, etc.) or salt (Potassium hydroxide, Zinc Chloride, etc.). The chemical agent is mixed with the raw material in a range of temperature of 300 to 800ºC. The derived Activated carbon will have various range of pore diameters known as Microporous, Mesoporous and Macro-porous. Post-Processing steps occur after the activation process Moreno- Piraján, and Giraldo (2013), Kienle and Bader (1984), and Kirk and Othmer (1992). They include washing the AC to remove ash content, sizing the produced AC into Power, Granule or Extrude. Also, Chemical Impregnation and Re-activation. Many researches have studied the production of activated carbon from various raw materials Brateka *et al.* (2013) and Wang (2012). Due to the low economical value and difficulty of utilizing the hull of sunflower seeds, (in this paper) Sunflower Seeds was used as a raw material one of the cellulosic wastes for the preparation of the activated carbon. The major components of the hull are lipids, carbohydrates and protein, where lipids represent 5% Moreno- Piraján, and Giraldo (2013), Kienle and Bader (1984) and Kirk, and Othmer (1992). AC has been used in different application including controlling the gasoline vapor emission and purification applications such as municipal and ground water treatment, water purification, landfill gas emissions, power plant, and precious metal recovery. It's also used to remove hazardous components in water, wastewater and gases. Moreover, it's used in various types of Air purification solutions include VOC removal and odor control Abatan *et al.* (2019) and Black *et al.* (1965).

Phosphorus is one of the most abundant elements in nature. Compounds of phosphate are found in natural water, domestic wastewater and in industrial water. In the later, they are either produced from fertilizer plants or irrigation water and they are known as ortho phosphate, or they are produced from the discharge of waste powders or household waste water containing washing powders known as polyphos- phate. Since all these species help the growth of algae and lichens abnormally in the water, it is an important nutrient of aquatic plants. In addition, they affect the concentration of oxygen dissolved in the water and finally it affects the aesthetical Suteu *et al.* (2011).

Phosphate compounds exist in the form of soluble substances, suspended, or Deposition materials.

Materials and Methods

Preparation of Activated Carbon.

A mixture of sunflower seeds was collected from several areas Cafes and Homes. The mixture was the raw material for the preparation of activated carbon by chemical activation method using H_3PO_4 as chemical agents. The preparation of activated carbon was in three stages:

Stage one: the mixture was pre-processed to be ready for activation process through washing with distilled water for several times until the dust and impurities were removed, then dried at a temperature of 80 degrees Celsius for 24 hours using a laboratory Oven Moreno-Piraján and Giraldo (2013), Kienle and Bader (1984), and Kirk and Othmer (1992).

Stage two: the mixture was impregnated with the chemical agent at a ratio of 1: 3 and kept for 3 days. The prepared sample was filtered, washed with distilled water and dried at 100 °C for 1hr. Then, it was burned at 600 degrees Celsius.

Stage three: the prepared activated carbon was washed with distilled water to remove the remained ash in the sample then examined to obtain the total surface area of carbon per 1gm Brateka *et al.* (2013), and Wang (2012).

Preparation of Phosphate Stock Solution

Phosphate was chosen to study the adsorption properties of the prepared activated carbon. A 0.219 gm of the Phosphate was diluted in 1000 ml volumetric flask of distilled water to prepare a 50ppm Stoke Solution. phosphate characteristics and its structure are shown in table (1) and Figure (1) respectively

Table 1 : Characteristics of Methylene Blue dye

Molecular weight	136.086 g/mol
Molecular formula	KH_2PO_4
Absorbance	690 nm

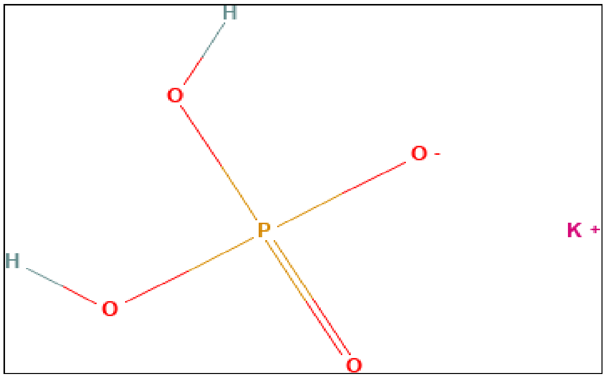


Fig. 1 : Structural formula of KH_2PO_4.

Adsorption Procedures

The experiment was carried out in a series of 100 ml of conical flask. Activated carbon concentration and a phosphate concentration were 0.5 g and 3ppm respectively.

The adsorption procedures have their own effect on the phosphate removal by shaker. The range of speed was between 100 to 300 rpm through a period of time between 30 to 120 minutes and a temperature range of 20 to 50°C. The samples were filtered by a paper filter and then absorbance was measured by spectrophotometer.

Isotherm studies

Adsorption isotherms show magnitude of material adsorbed per unit mass of adsorbent as a function of the equilibrium concentration of the adsorbate. The data are obtained to determine the specific mass of adsorbents that are calibrated with a known chemical concentration volume derived from experiments, by balancing the equilibrium of the mass, the resulting equilibrium concentration is measured in the solution: Siahpoosh *et al.* (2016).

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \qquad \text{...(1)}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \qquad \text{...(2)}$$

Where:

R% : Removal efficiency.

C_e, C_0 : Final & initial concentration of the solute respectively (mg/L).

m : Adsorbent mass (g)

V : Volume of solution

q_e : The amount of pollutant adsorbed per gram of adsorbent at equilibrium, (mg/g).

There is a lot of isotherm models, Langmuir and Freundlich isotherms will be discussed in this research Suteu *et al.* (2011)

Langmuir Model

The model of Langmuir adsorption shows the balance between the aqueous phase and the solid phase in the form of an opposite chemical balance between species Buffle and Stumm (1994). In the equation of adsorption there are three main hypotheses: (a) Adsorption capacity which is the same in all locations, (b) Adsorption occurs on localized sites without any interaction between the absorbed molecules, and, (c) a complete monolayer which is the highest possible absorption. Langmuir equation is illustrated below:

$$q_e = \frac{q_{max} C_e K_L}{1 + C_e K_L} \qquad \text{...(3)}$$

Where

q_e : Fraction of the mass of adsorbate to the mass of adsorbent (mg/g)

q_{max} : Maximum adsorption capacity for the monolayer (mg/g)

C_e : Adsorbate concentration remaining in the liquid phase at equilibrium (mg/L)

K_L : Langmuir equilibrium constant (L/mg).

The Langmuir constant describes the relationship between adsorption and desorption of molecules on the surface and relates the affinity of the adsorbent to the sorbent. Depending on the slope, and high K_L indicating high adsorption at lower concentrations. When equation (3) is linearized, the adsorption parameters can be determined.

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

Plotting C_e/q_e versus C_e generates a graph with a slope of $1/q_{max}$ and an intercept of $(1/K_L{*}q_{max})$)

Freundlich Isotherm Model

The Langmuir model assumes that the energy is equal to all surfaces and does not depend on the degree of coverage. In fact, the adsorption capacity varies because the surfaces are heterogeneous. So Freundlich Isotherm found it.

$$q_e = K_F C_e^{1/n} \qquad \text{...(5)}$$

Where

C_e : equilibrium concentration of adsorbate in solution after adsorption , mg/L

q_e : mass of adsorbate adsorbed per unit mass of adsorbent , mg adsorbate/g adsorbent

K_F : Freundlich capacity factor

1/n : Freundlich constant 1

Linearization of equation (5) of Freundlich can be equated as follows:

$$\log q_e = \log K_F + \frac{1}{n}\log C_e \qquad ...(6)$$

$\log K_F$: Interception factor.

Results and Discussion

Preparation if activated carbon

In the process of chemical activation, many parameters have diverse important effects on final activated carbon properties where the surface area was 496 m^2/g.

(i) Optimization of impregnation ratio (R):

Impregnation ratio (R) plays an important role in influencing the surface area produced by the prepared activated carbon. It is known that chemical activation agent (H_3PO_4) penetrate the carbon structure chemical changes) causing pores to form which lead to formation the activated carbon, when the chemical agent increased the surface area increased until reached the optimum.

(ii) Optimization of impregnation time:

The duration of impregnation has an important role in the formation of carbon and activated so it must take time to reduce volatiles and moisture which helps in the formation of pores.

(iii) Optimization of carbonization temperature (T_c)

Carbonization temperature showed a significant impact on activated carbon produced through a series of destructive reactions that results in the removal of volatiles from raw materials and the formation of porous carbon. the destructive reactions and removing of volatile materials could not happen at lower temperatures, but at higher temperatures, tar will be formed and consequently clog the pores.

Absorption of phosphate

(i) Effect of Contact Time

Contact time is as essential factor that needs to be determined in batch adsorption process. The effect on the adsorption process of the phosphate is shown in Fig. 1. At the beginning, removal of M.B increased rapidly on external surface of activated carbon due to the presence of high number of active adsorption sites. After 90 min, the adsorption reaches the equilibrium and take place on the internal surface as the remaining sites on the surface are difficult to be occupied [19]. Fig1 shows the effect of contact time on the removal percentage.

(ii) Effect of Agitation Speed

Agitation speed is one of the important parameters in adsorption phenomena due to its effect on the distribution of adsorbent (activated carbon) in the solution of phosphate. The effect of agitation speed studied at different range of agitation speeds. The figure below shows the removal of phosphate increases with the increase in agitation speed. This behavior due to the increase in turbulence and the decrease in boundary layer thickness around the adsorbent particles. Fig. 2 shows the effect of Agitation Speed on the removal percentage.

(iii) Effect of Temperature

This effect was investigated at (20-50 ^{o}C). Fig. 3 shows the removal percentage of M.B decreased from 90% to 76%, after increasing the temperature from 20 to 50oC. Increasing the temperature is known to decrease the diffusion rate of the adsorbate molecules across the outer boundary layer and internal pores of the adsorbent particle, yielding to the decrease solution viscosity. Fig3 shows the effect of Temperature on the removal percentage.

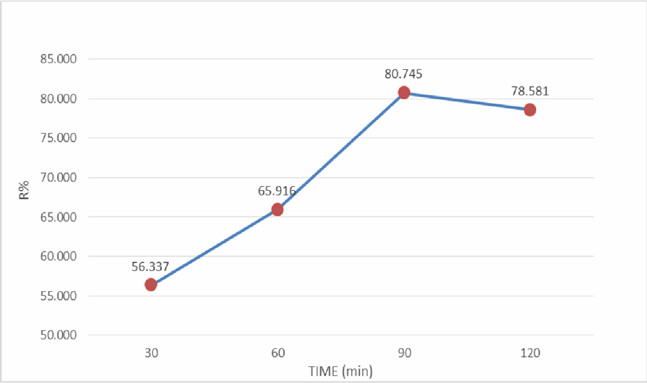


Fig. 1: Relation between Contact Time and Removal Percentage

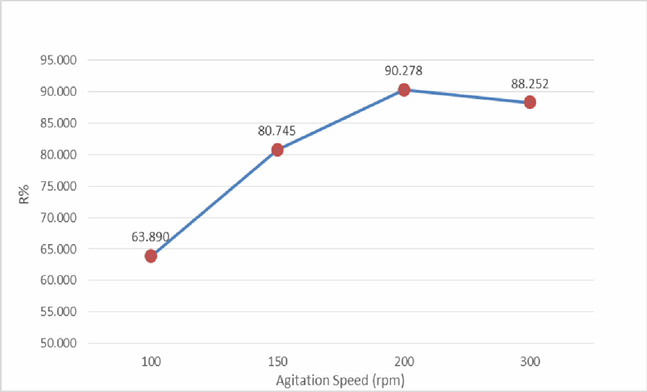


Fig. 2: Relation between Agitation Speed and Removal Percentage

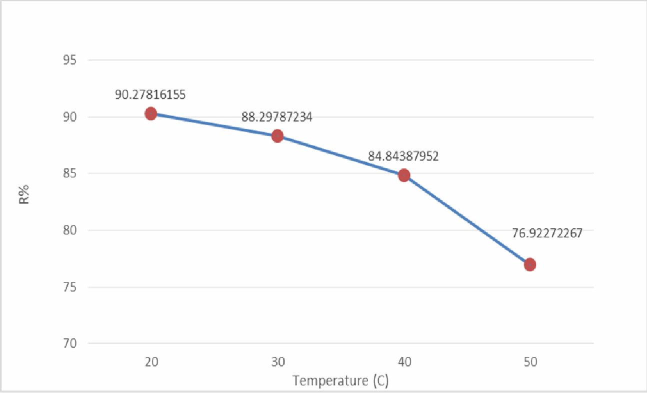


Fig. 3: Relation between Temperature and Removal Percentage

FTIR Test

Functional groups that have been adsorbed by phosphate are scanned using Fourier transform infrared spectra (FTIR). The tests on the activated carbon are carried out within a range of 4000-1500 cm^{-1} of the wave number. The figure shows wave number before and after adsorption of Phosphate. The groups function is one of the most important evidence for understanding of adsorption.

Activated carbon FTIR spectra before and after adsorption states of M.B showed the peaks of O–H shifted from (3433.29 to 3425.58) cm^{-1} and an intensive peak appeared at 1581.65 cm^{-1}. Bending vibration of adsorbed H_2PO4- in the spectrum of the absorbed phosphate, indicating that phosphate groups were replaced by the existing surface hydroxyl. In Addition, one weak peaks appeared at 1219.01cm^{-1}, which were assigned to P-O bands variation. It was evident that the surface hydroxyl groups of the adsorbent played an important role in the phosphate adsorption process. FTIR test is shown in Fig. 4.

SEM Test

In the figures 5 and 6 we observe, the activated carbon before adsorption can clearly see the surface, but after the adsorption process the surface has become fully covered and this indicates that the Phosphate has occupied a place on activated carbon surfaces. SEM test is shown in Fig. 5 and Fig. 6 for Before and After Adsorption Process.

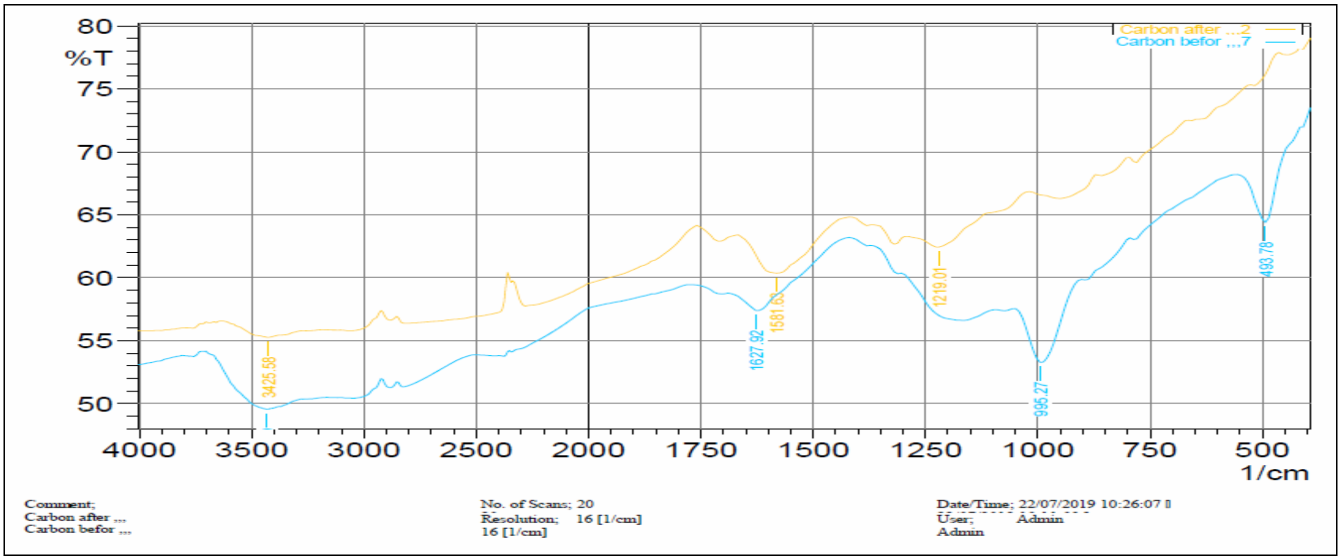
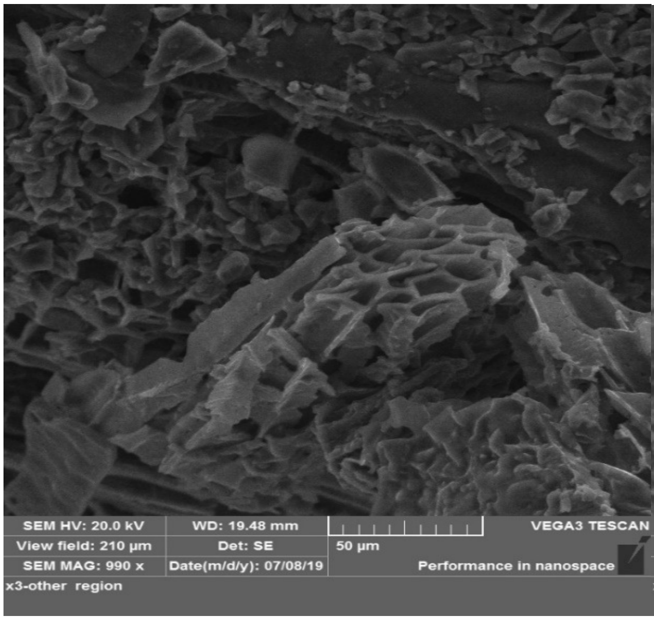
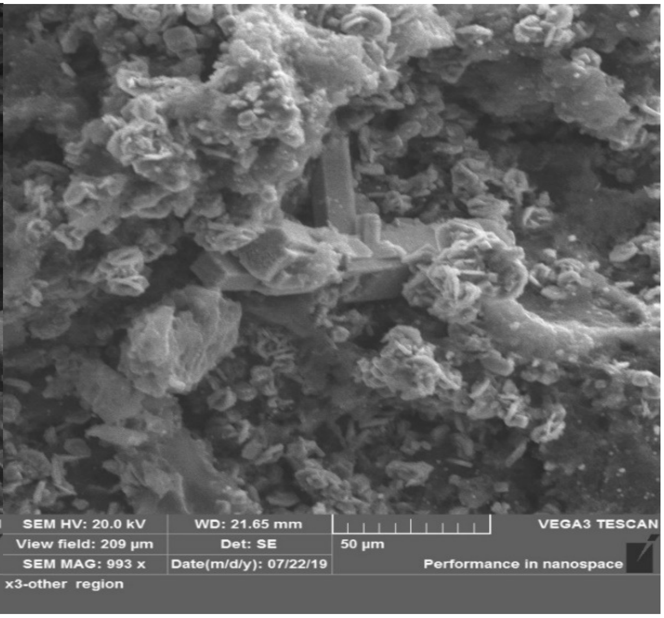


Fig. 4: FTIR Spectra of Fresh Activated Carbon and Activated Carbon Loaded with Phosphate





Iso Thermal

Results show that adsorption isotherm of phosphate was described very well in Freundlich than Langmuir isotherm where R2 use to determine that. In Freundlich isotherm plot of Ce vs Ce/qe are shown in figure and value of R2 and maximum capacity are (0.7539) (2.11 mg\g) respectively. While plot of logarithmic form of Ce vs log qe for Freundlich isotherm to know R2 where the value of R2 are (0.9104) as shown in figure 7 and 8. Table 2 shown the parameter of isotherm models.

Table 2 : Isotherm Parameters for phosphate Adsorbed by prepared activated carbon

Model	Parameters	Phosphate
Langmuir Isotherm	q_m (mg/g)	2.11
	KL (L/mg)	0.894
	R2	0.7539
Freundlich Isotherm	KF (mg/g) (L/mg) 1/n	1.0444
	n	1.891
	R2	0.9104

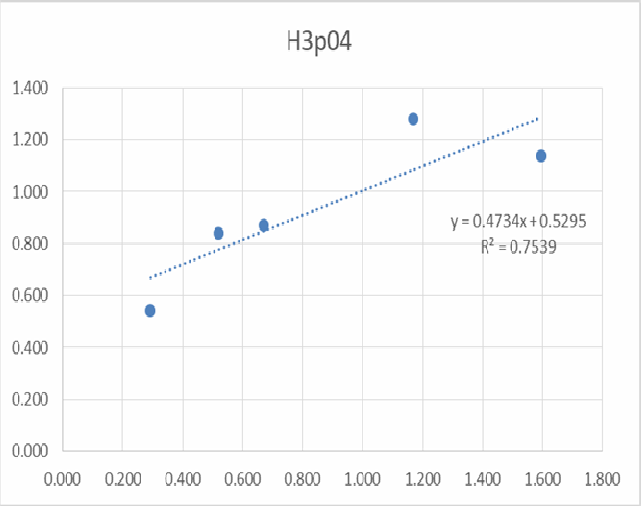


Fig. 7: Langmuir isotherm

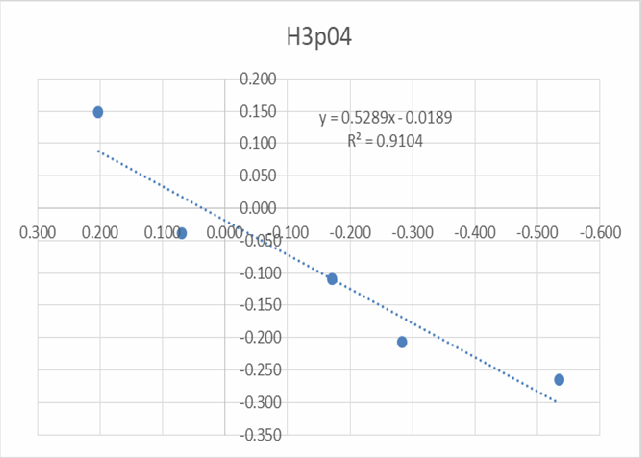


Fig. 8: Freundlich isotherm

Conclusion

Activated carbon of large surface area were prepared from sunflower seeds husk by chemical activation using H3PO4 as chemical agent. Preparation of activated carbon was determined by a set of conditions where the highest surface area was used for adsorption of phosphate and the highest removal rate was 90.27% at t=90min,speed= 200rpm, 20oC,concentraion= 3ppm,does= 0.5 g activated carbon.

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