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Ege universitesy

Faculty of engineering

Department of chemical engineering

Diploma project

Adsorption of 2,4-D and Cu from aqueous solution by activated carbon developed from olive stones

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Abstract:

Due to the usage of commercial activated carbon with high associated costs, attempts have been made to find inexpensive alternative activated carbon precursors as waste materials. Olive stone is among the most widely preferred agricultural wastes for the economical production of activated carbon. In this study, olive stones obtained from an oil factory located in Kuyucak, Aydın was used as raw material for the production of activated carbon via chemical activation which reduced the formation of tar and other by-products, thereby increased the carbon yield. For this purpose, phosphoric acid, potassium hydroxide and zinc chloride were retained as dehydrating agents. The impregnation ratio, defined by the weight ratio of the impregnants to olive stones, was kept constant as 1:1.5. The samples were carbonized in a furnace heated to 600˚C (2h) under a constant flowing nitrogen atmosphere. The chars obtained were cooled at room temperature and the weight losses due to pyrolysis were determined. Characteristics of the activated carbon were conducted and the pesticide adsorption capacity of each modified-sorbent was also determined separately. It is concluded that chemical agents enhance the quality and quantity of the activated carbon produced.

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Her gün okula gitmek için bana enerji vermek için benim kraliçe teşekkür ederim.

And finally to my family for gave me the opportunity of study here with their economical and moral support.

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A. Apendix

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1. Related studies and antecedents

The activated carbon is being developed in the last decade as an efficient adsorber of different compounds, fixing them on the surface in order to be eliminated or recovered from a liquid phase.

The research is focusing now in find cheap raw materials that can supply the great amount required for obtain the adsorbent. Is know that the residues of any industry is a not expensive product that can be acquired even for free, following that line the agricultural waste can supply this raw material at cost and amount necessary for an industrial manufacture of activated carbon.

The activation of this raw material can be made using heat directly (physical way) or using and activator before the pyrolysis process (Chemical activation). This activator use to be and acid, the most common are ZnCl2 (Aygun et al. (2003)), H3PO4 (Baccar et al. (2009)), and KOH (Ubago-Perez et al. (2006)) (Figure 1.1).

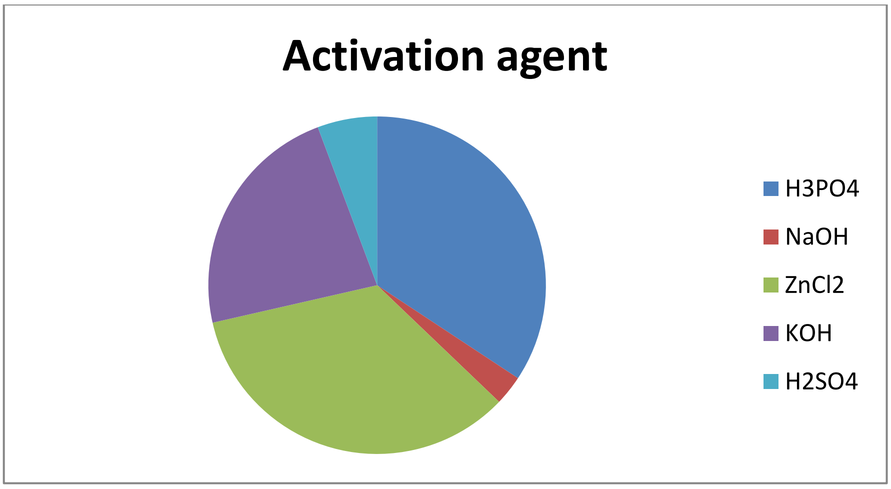

Figure 1.1

Focusing at the compounds removed, this adsorbent is focused in heavy metals like Cu ((Yahaya et al. (2010)), Hg (Zabihi et al. (2010)), Pb (Xu and Liu (2008)) Cd (Kula et al. (2008)), and also dyes (Oliveira et al. (2009)) (Figure 1.2).

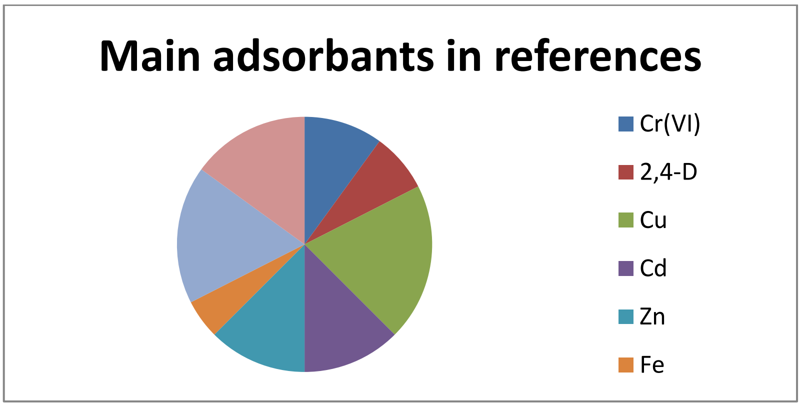

Figure 1.2

Is easy to find several researches t ut this topic (Figure 1.3). Olive stones (Zabaniotou et al. (2007), Kula et al. (2008)), rice husk (Kalderis et al. (2008), Yahaya et al. (2010)) and Wallnut shells (Martínez et al. (2006), Zabihi et al. (2010)) are the most common precursors than you can find at the bibliography.

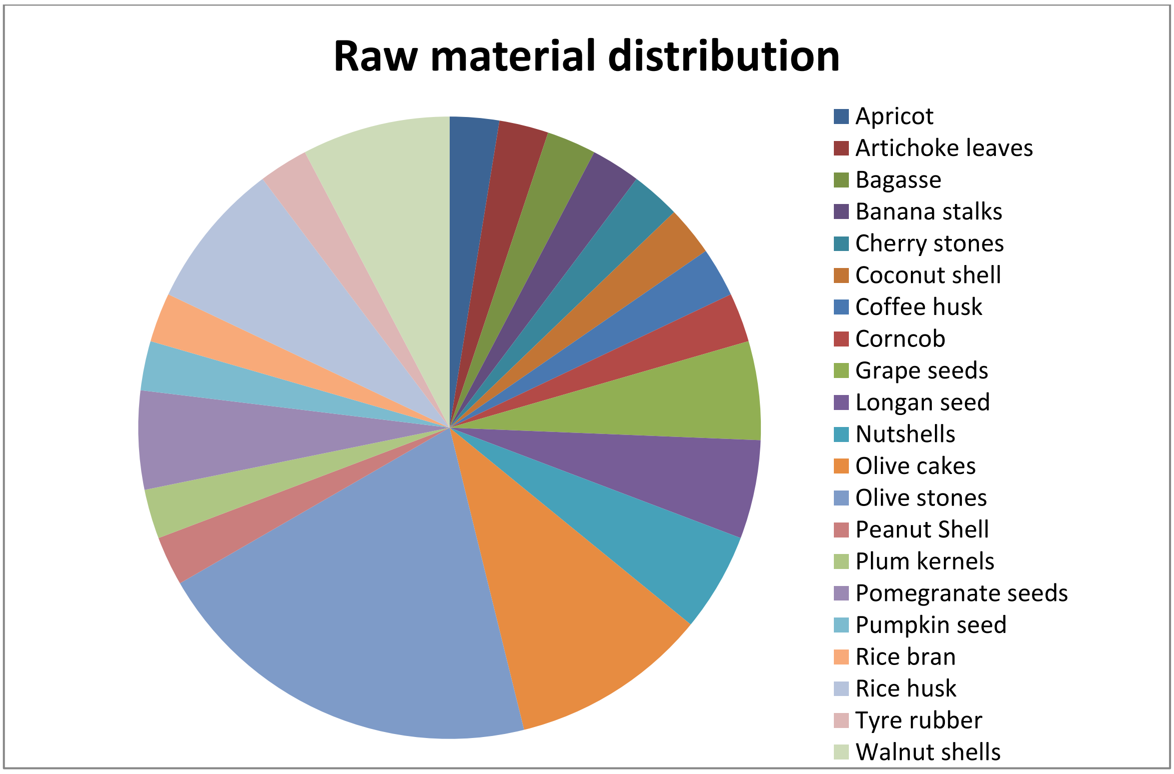

Figure 1.3

Our target is prove that the raw olive stones can be used for manufacture activated carbon and uses this for adsorbate the pesticide 2,4-D from an aqueous solution in a batch process. The chemical activation shows quite good results in this way, phosphoric acid with a qmax of 250mg/g (Njoku and Hameed (2011)), KOH with 249mg/g (Njoku et al. (2013)) and zinc chloride with 122,37 mg/g (Salman et al. (2011)) are the most used acid for carried this chemical activation process.

This study will show the expected results for the absorbance of 2,4-D and copper in an activated carbon that avoid the impregnation process in its manufacture and is introduced directly in the reactor for the pyrolysis process. The results will provide us important values in order to compare them with the impregnated ones regarding at bibliography and also the possibility of used this raw material directly saving the cost of the amount of acid needed in the other studies. We expect less adsorbance values regarding at the qmax.

2. Experimental procedure:

2.1 Equipment list:

2.1.1: Laboratory equipment:

-Erlenmeyer glass (250mL) x23

-Vickers glass (100mL) x30

-Volumetric flask (100ml) x10

-Volumetric flask (2000mL) x2

-pHmeter (WTW pH330)

-Filter paper (Sartorius stedim biotech 388)

-Balance (AND HM-200. Max 210g, d=0.1mg)

-Shaker x3 (Selecta unitronic OR x2 and Memmert WNB 14)

-UV spectrometer (PG instruments LTD T80+)

-Different volume pipets (10mL,25mL,50mL)

2.1.2: Additional equipment:

-Adiabatic reactor provided for the science department of Ege university

-Atomic absorption device.

2.2 Timeline diagram of the experimental procedure:

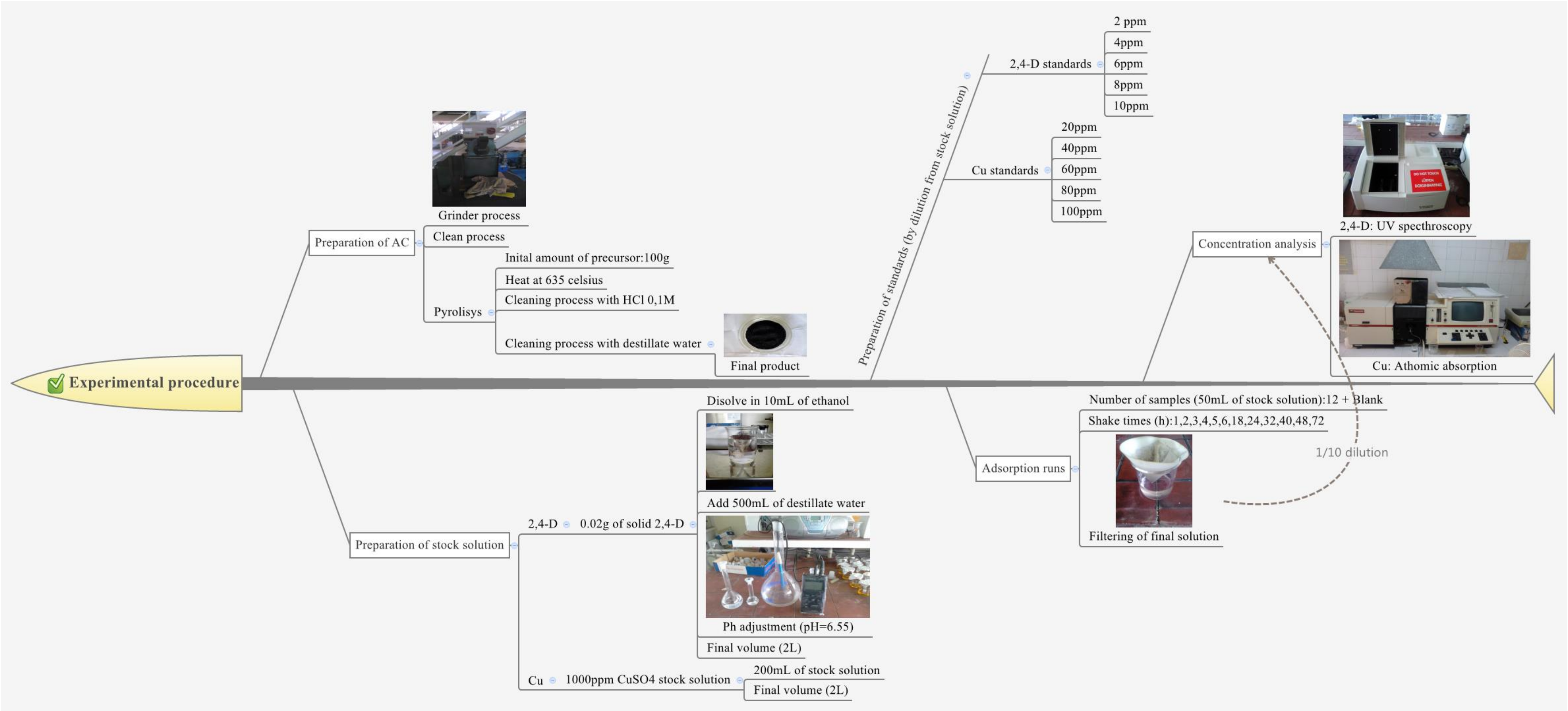

Figure 2.1

2.3 Activated carbon manufacture:

The olive stones used as raw material are provided by the agriculture department of Ege University.

The seeds are put through a milling process to reduce it to dust; this process increases the surface of the material and helps the efficiency of the following steps of the manufacture. This dust is collected and cleaned with distillate water for remove the impurities and obtains a pure precursor for the pyrolysis process.

The cleaned olive dust must be dried in an industrial oven at 120°C for 24 hours for ensure that the water is completely removed.

The next step is the pyrolysis process. The reactor used is an adiabatic batch reactor modificated for provide a constant flow of nitrogen that will be supplied while the reaction is carried. This flow ensures an inert atmosphere inside the reactor avoiding the presence of combustion gases that can be adsorbed by the product decreasing its efficiency in later uses. The outlet gas flow must be put through chloridric acid solution in order to absorb dangerous residual compounds that should be dropped to atmosphere.

Regarding at previous studies (Yakout et Sharaf (2011), Ubago-Perez et al. (2007), Xu and Liu (2008)) the final temperature will be set at 635 °C. The process takes about one and a half hours to reach this temperature with an average heating rate of 7°C/min. Once the final temperature is reached we stop the heat supply and wait until the reactor cools by itself.

Once the reaction is finished, the product is retrieved from the reactor. There is a weight loss that will be measured due to carbonization and combustion of the reactant. This weight loss will be useful by the time we wanted to calculate the yield of the process.

Once the product is ready, the cleaning process is being carried. The product is cleaned with a solution of chloridric acid with a concentration of 0.1 M. This process is necessary for remove the ashes and residues produced during the pyrolysis in order to avoid the contamination of the flow that is going to be put in contact with the activated carbon during the adsorbance process. Due to that, the remaining HCl after this step should be removed too, for that purpose we clean it with distillate water. The control variable that ensures that all the acid has been removed is the pH. It will be measured at the outflow of the cleaning process that will be done once the outlet pH value reaches 6,55 or higher.

Again, the final operation will be dry the product using an industrial oven that operate at 120°C for one hour.

2.4 Stock solution preparation:

The stock solution of 2,4-D should be prepared according with the necessary amount of it that is going to be use in the adsorption process. The following table shows that the required volume is 1950mL, so a 2L vessel is going to be used.

	Number of units	Volume (mL)	Sets	Total volume (mL)
Samples	13	50	3	1950

The remaining 50mL will be used for prepare standards that will be needed at UV analysis.

The standard solution has a concentration of 100ppm (mg/L) (Njoku and Hameed (2011)), that means that for a final volume of 2 liters 0,02 grams of pure 2,4-D will be measured.

2,4-D has a low solubility in water due to its low solubility constant, the dilution process requires that the solid 2,4-D was diluted in pure ethanol before add it to final water solution. For this purpose 10 mL of ethanol are used for make an initial dilution.

Once the dilution is done, it should be added drop by drop to the aqueous solution. The greater amount of water, the better the dilution will be carried.

A neutralize process is also necessary due to 2,4-D use to precipitate ruining the stock solution. Solutions of HCl (0.1M) and NaOH (0.1M) will be used for the neutralize process that should show a final pH above 6,55.

After add all the ethanol solution and reach the neutralize point, the final required amount of solution (2L) will be reached adding more distillate water.

For copper solution, the desired concentration is going to be 1000ppm, that means 1 gram os copper per liter of solution. The required amount is the same as in 2,4-D adsorbance experiment, 1950mL of stock solution for samples and 50mL for prepare standards using a dilution process. The copper will be provided by a solid copper sulfate, the calculation shows that the necessary amount of copper sulfate is -----grams.

This amount of copper sulfate is added to a little amount of distillate water till it dissolves completely and after that more distillate water is added for reach the final 2L of solution. The sulfate anions in the solution become it in a weak basic solution, the required optimum pH for the experiment is five (Yahaya et al. (2010)), so solutions of HCl (0.1M) and NaOH (0.1M) will be used for reach this final value.

2.5 Standards preparation:

Standard solution is a critic resource for obtain good accurate concentration results. This solution will be measured using the same device that samples and it use same stock solution to be made. Comparing the adsorbance values of this solution with the values showed at sample analysis a real concentration value is going to be obtained.

The range concentration of the standard should go from cero (total adsorption) to the value of the stock solution (null adsorption). This top value is too high for be measured at the available devices (100ppm for 2,4-D and 1000ppm for Cu) so a dilution of 1/10 is going to be done at samples. This means that new top values of standard solutions will be 10ppm for 2,4-D and 100ppm for Cu. Some extra values could be added for ensure a well approached calibration curve.

All the standard solutions will be done in a 100 mL flask. A measured amount of stock solution will be added and final volume is going to be filled with distillate water following the values of the next table.

Adsorbent	Concentration	Stock solution volume(mL)	Distillate water volume (mL)
Cu	20	2	98
	40	4	96
	60	6	94
	80	8	92
	100	10	90
2,4-D	2	2	98
	4	4	96
	6	6	94
	8	8	92
	10	10	90

Plotting the adsorbance values of this solutions and approaching the plotted points to a linear distriburion a function that link adsorbance values with concentration is obtained.

Supporting on these functions the adsorbance values given by the devices became real concentration values.

2.6 Adsorption experiments:

The adsorption analysis carried in this research is a kinetic experiment focused in obtain the equilibrium time for the adsorbance of the activated carbon in a batch reactor operating at desired conditions.

This equilibrium time is the value in time units that indicates the completely saturation of the activated adsorbant. This value is important for future industrial processes due to shows the time at the adsorbant should be replaced or desorbed and regarding to more experimental work is critic for the equilibrium experiments that show the different final values of adsorption for different initial concentrations of adsorbate. The equilibrium time will be reached once the adsorbance value get constant with time.

The bibliography show that the expected equilibrium time will be between 30 and 48 hours for 2,4-D adsorbance at pH 7 and initial concentration of 100ppm (Salman et al. (2011)).

The sample times for this experiment will be 1,2,3,4,5,6,18,24,32,24,48,72 plus a blank sample and 3 sets will be done. This means that 36 samples will be used in the kinetic experiment.

The amount of activated carbon used in each sample is 0,01 grams and it is placed in an Erlenmeyer vessel. 50mL of stock solution will be added to the activated carbon next to the begin of the experiment. For simulate the stirred batch reactor conditions a shaker (Figure 2.2) device will be used.

Figure 2.2

The shake rate will be fixed to 90rpm and the temperature of the process is set to 25°C.

The samples will be retrieved one by one once they reach the time set previously. In order to separate the activated carbon from the treated solution all of the samples will be filtered. This filter process ensures a good aim by the time the concentration was calculated.

UV analysis is going to be used for determine the final concentration of 2,4-D after the adsorbance. For copper experimentes atomic absortion device will be necessary.

Comparing this values with the calibration curve obtained using the standards the final concentration is calculated with a negligible error.

2.7 Ash content studies:

The ash content analysis of activated carbon shows the residual compounds (Mg, Ca, Si, Fe, Salts) that remains in the adsorbent after manufacture.

For calculate this percentage of ashes the carbon is heated till a completely combustion at an oven that heats it at 900 °C. The initial amount of activated carbon should be measured in order to compare it with the remaining residue (ashes) after carbonization. With a simple arithmetic calculation relating previous and subsequent weight the ashes content is obtained in percentage

3. Results and discussion:

3.1 Activated carbon develop:

The initial value of activated carbon precursor is 100 grams. It will be added into the batch reactor. The reactor will be closed and the adiabatic condition will be ensured with special low thermic conductivity foam.

The inert atmosphere is reached with a continuous flow of nitrogen with a flow rate of 23mL/min (Yeddou et al. (2010)). This flow is depurated at the output stream of the reactor using diluited acid and basic solutions.

The reaction takes about one hour and the heating rate change at the different ranges of temperature.

Once the results are plotted in a graph (Figure 3.1), the conclusion is that the greater heating rate is reached when reaction is in the middle interval from begin to final set point at 635°C.

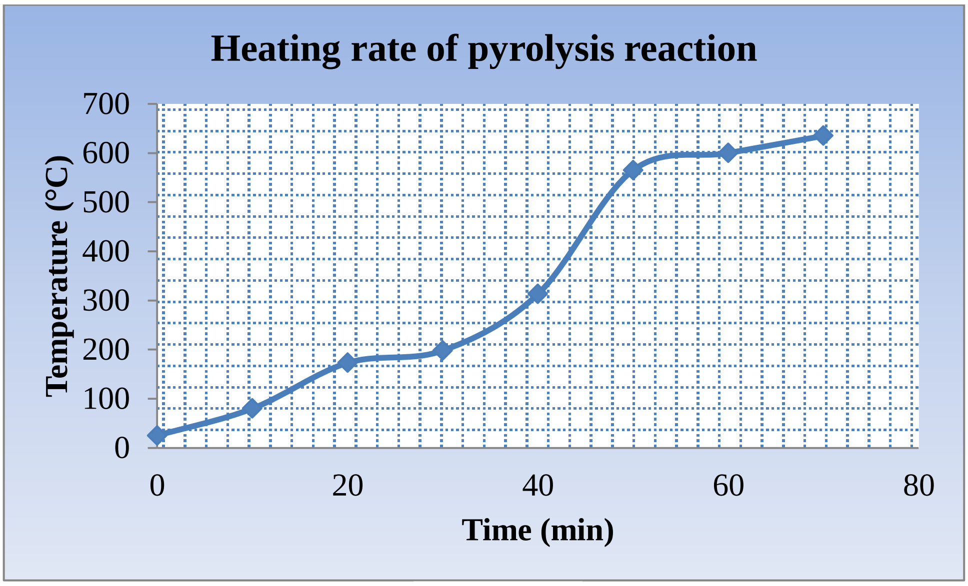

Figure 3.1

The final amount of product at the reactor is 25,67 grams, that means that the efficiency of the process is 25.67% with a weigth lost of 74.33.

The target of carbonization process is increase the surface of the activated carbon, due to this the expected absorption is going to be greater for high surface activated carbons (Ahmad et al. 2007).

The surface area of the activated carbon is determined by nitrogen adsorption in the surface of the adsorbant (BET analysis). This BET area is expressed in square meters of surface per gram of adsorbant.

Searching at references and previous studies, the following graphic has been developed for determine the range of surface area of our activated carbon according to the control variables temperature and carbonization time.

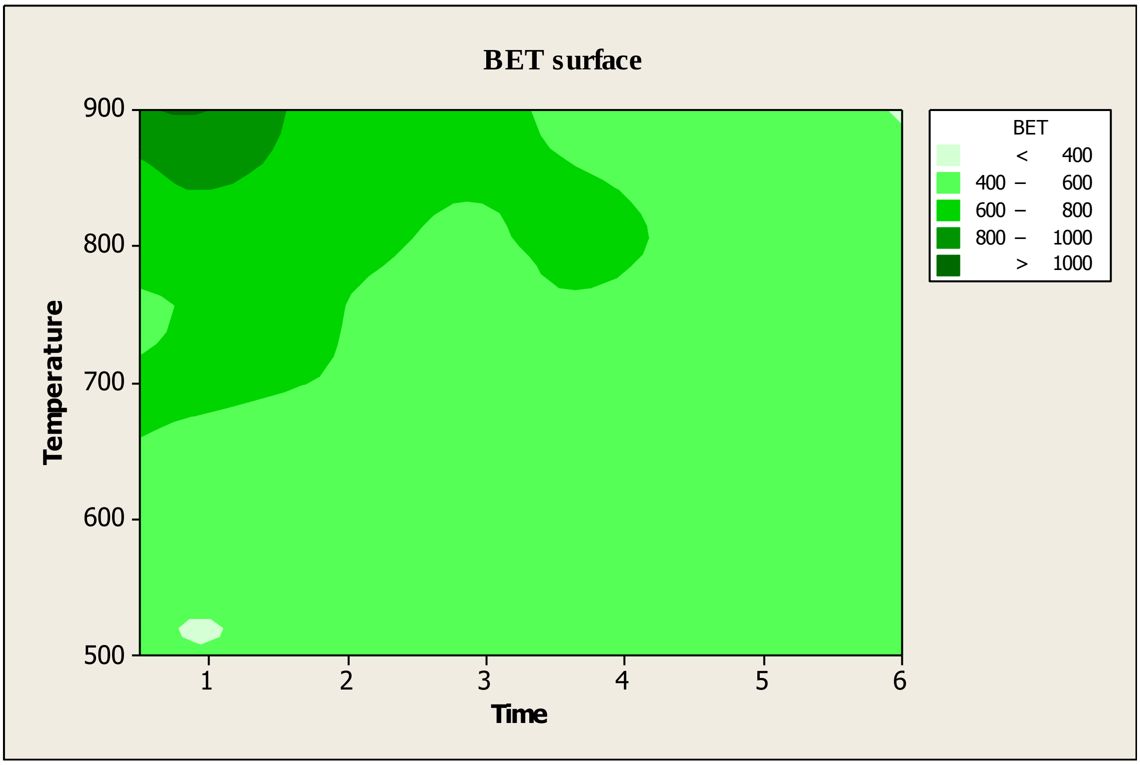

Figure 3.2

Analyzing the graphic (figure 3.2) is observed that higher temperature produce a higher surface area in the product (Aljundi and Jarrah 2008). A similar result can be obtained for lower temperatures increasing the carbonization time, but for long periods of carbonization results decreases due to degradation and destruction of the particles of activated carbon.

The process for this experiment was fixed for a final carbonization temperature of 635°C that is reached in 1,5 hours of carbonization process. Comparing it with the plot showed above the surface area is going to be contained in the 400-600 m^2/g range. The final product is showed in the following picture (Figure 3.3).

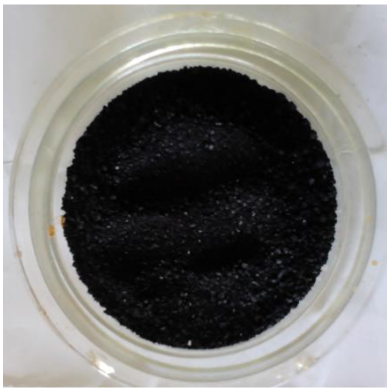

Figure 3.3

3.2 Adsorption experiments:

3.2.1 Kinetic study for 2,4-D:

50mL of stock solution was added to 0,01 grams of activated carbon and put into the shaker at a set temperature of 25°C.

The selected times for sample remove are 1,2,3,4,5,6,18,24,32,40,48 and 72 hours. In order to collect all the information and compare it, the following plot was developed:

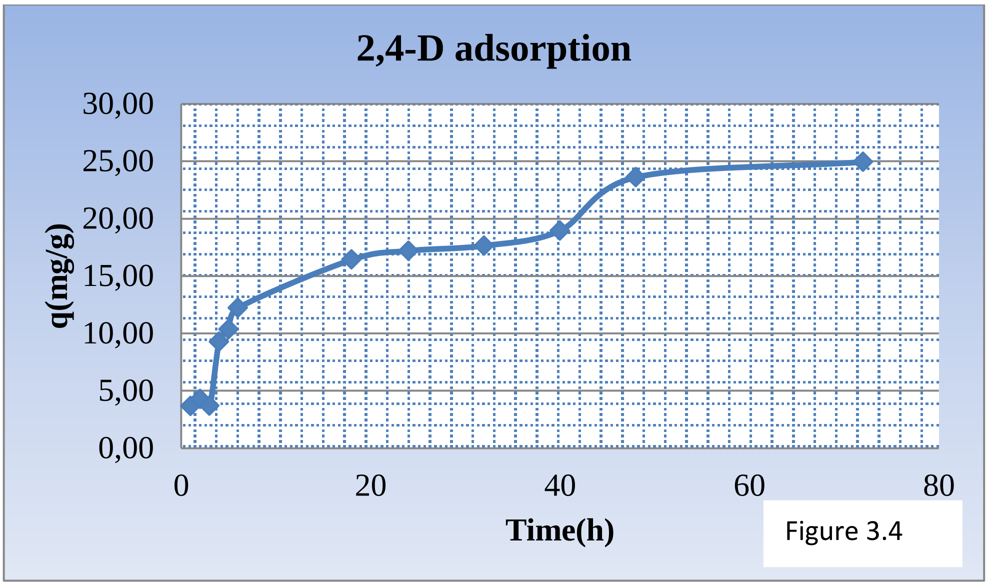

Figure 3.4

The final values show a maximum adsorbance value (qmax in mg/g) 24,94 mg/g with an equilibrium time of 46 hours.

Due to these experimental values don’t fit with the expected asymptotic curve, a regression adjustment will be done using Minitab as math tool for this purpose.

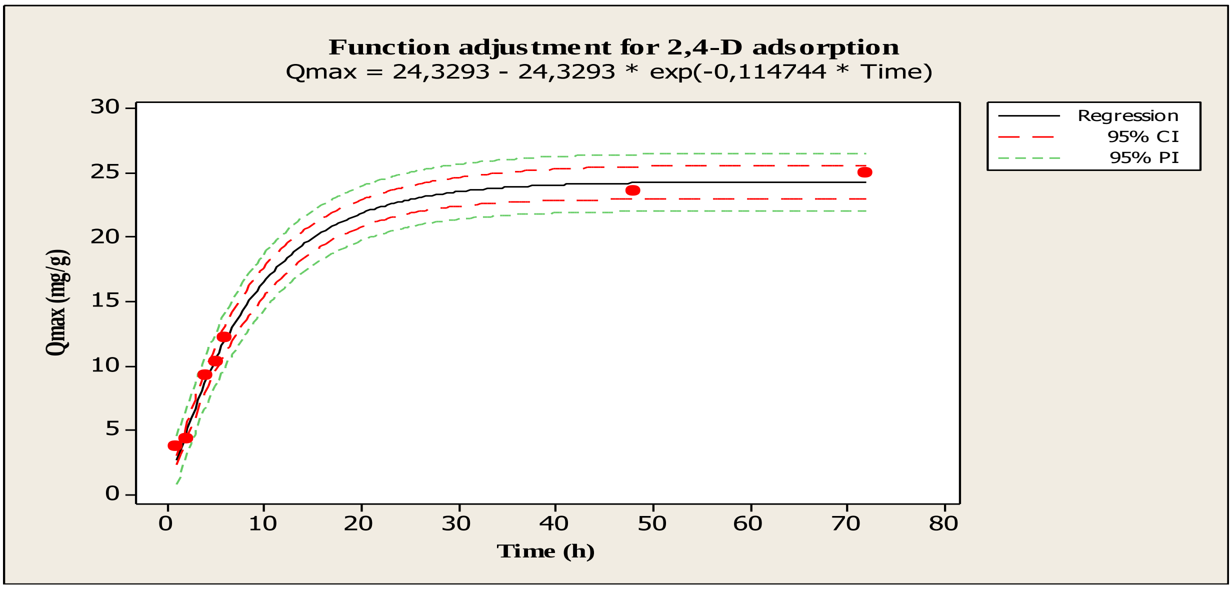

Figure 3.5

This graphic shows the theory function that drives the process according with the displayed data. The confidence interval and Predicted interval are plotted also and indicate the region where 95% of the real values for this time point will be found.

The function is an asymptotic curve according to the following ecuation:

Q = 24,3293 - 24,3293 * exp(-0,114744 * Time)

With a basic math analysis the value of Qmax can be found for an infinite time as 24,33 mg/g.

For find the equilibrium time is assumed that as time increases the value of adsorbance should be almost constant. Fixing this differential value at 0,1 and obtaining the time value for this point equilibrium is reached at 49,9 hours.

3.2.1b Determination of kinetic parameters:

A) Pseudo-first order kinetic:

The pseudo-first order kinetic is defined for the paremeters q_e and k_1. For obtain this values a graphic plotting $\log(q_e\text{-}q_s)$ vs time should be done (Apendix 3.1).

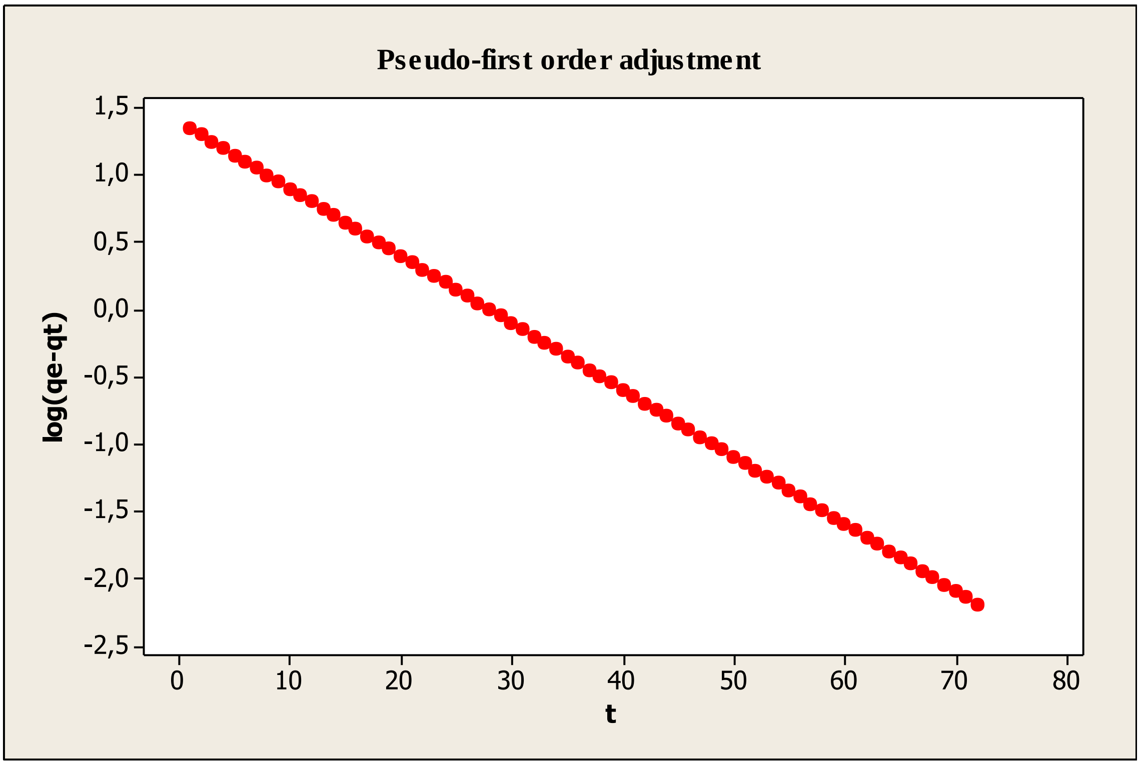

Figure 3.6

The ecuation function is log(qe-qt) = 1,39 - 0,0498 t with a $R^2$of 1. Q_e value is equal to 24.547 and 0.1147 is obtained for k_1.

B) Pseudo-second order kinetic:

The pseudo-second order kinetic is defined for the paremeters q_e and k_2. For obtain this values a graphic plotting t/q_s vs time should be done (Apendix 3.2).

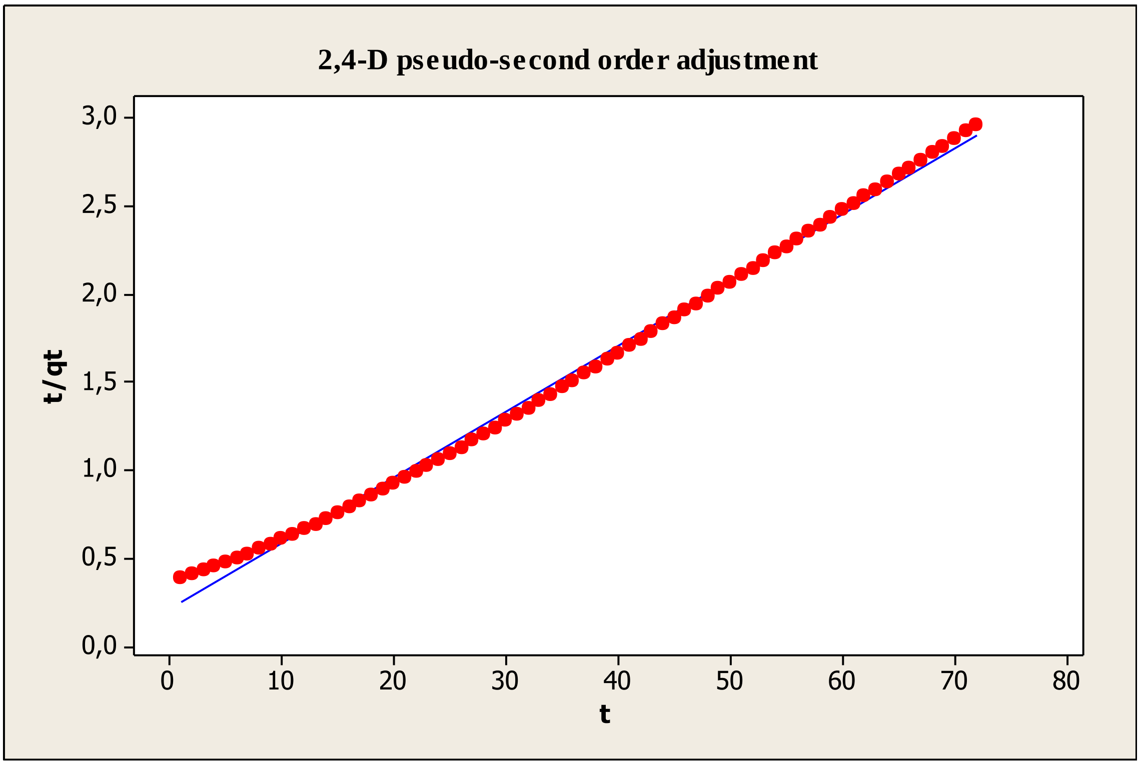

Figure 3.7

The ecuation function is `t/qt = 0,205 + 0,0374*t t`with a $R^2$of 0.996. Q_e value is equal to 26.737 and 0.00682 is obtained for k_2.

3.2.2 Kinetic study for Cu(II):

Following the same procedure as 2,4-D kinetic analysis, 50mL of copper stock solution is mixed into Erlenmeyer with 0.01 grams of activated carbon. The sets were also scheduled for 1,2,3,4,5,6,18,24,32,40,48 and 72 hours.

The concentration values of copper are too high at samples, but this is due to the function that relates atomic absorption results with real concentration has a low R square. But regarding at references (A.2) and assuming that the error is proportional for all values and differential calculations are done, the final q values should be acceptable.

The plots for q values and removal percentage are showed below:

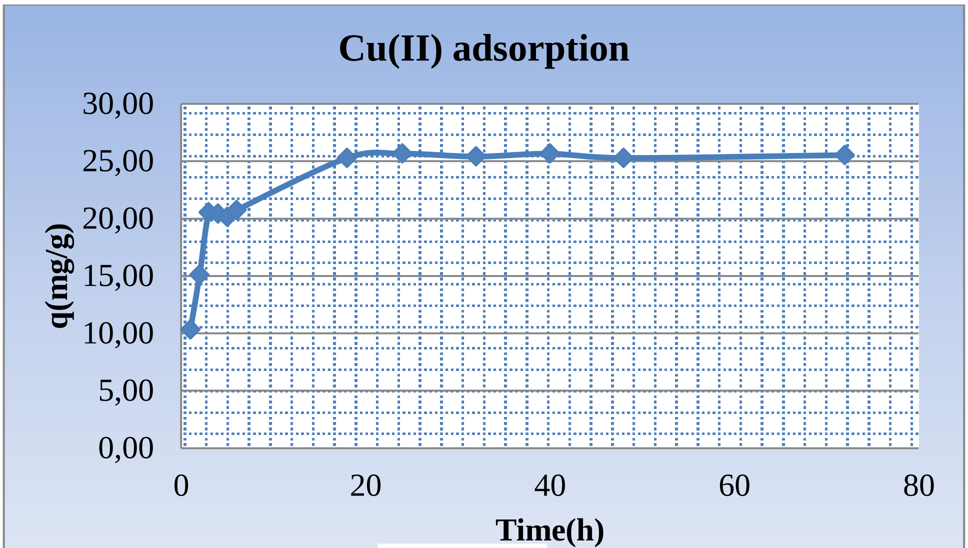

Figure 3.8

The final q value is 25,6 mg/g with an equilibrium time of 22 hours.

As happened with 2,4-D experiment, these experimental values don’t fit with the expected asymptotic curve, again, a regression adjustment will be done using Minitab as math tool for this purpose.

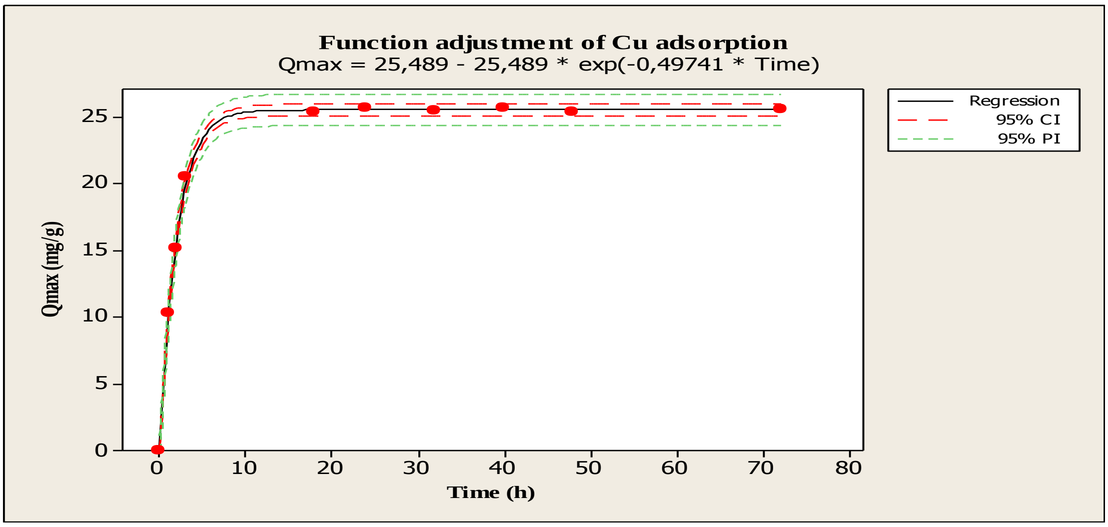

Figure 3.9

The function obtained is:

Q = 25,489 - 25,489 * exp(-0,49741 * Time)

Qmax of the adsorption process is found again at the infinite limit of the function being this value 25,49 mg/g.

The differential value of 0.1 from the maximum value is taken as equilibrium time and is reached at time equal to 11.1 hours.

3.2.2b Determination of kinetic parameters:

A) Pseudo-first order kinetic:

The pseudo-first order kinetic is defined for the paremeters q_e and k_1. For obtain this values a graphic plotting log(q_e-q_s) vs time should be done (Apendix 3.1).

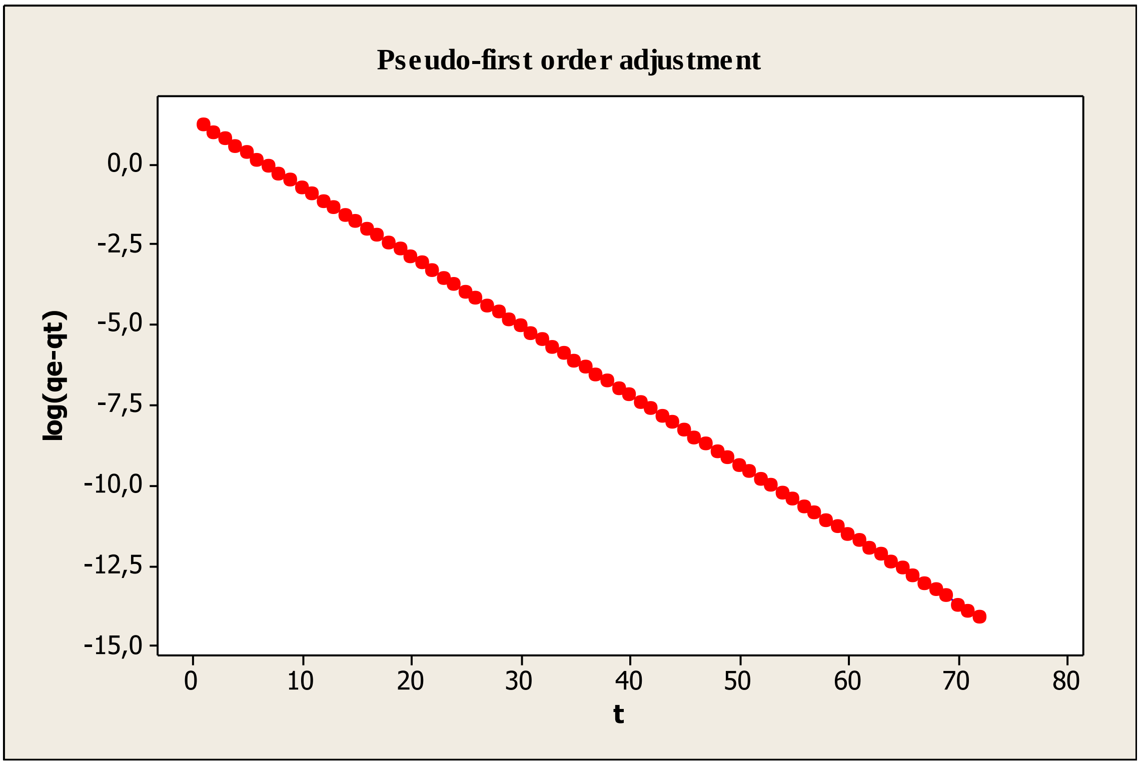

Figure 3.10

The ecuation function is `log(qe-qt) = 1,41 - 0,216 t`with a $R^2$of 1. Q_e value is equal to 25.7and 0.0.497 is obtained for k_1.

B) Pseudo-second order kinetic:

The pseudo-second order kinetic is defined for the paremeters q_e and k_2. For obtain this values a graphic plotting t/q_s vs time should be done (Apendix 3.2).

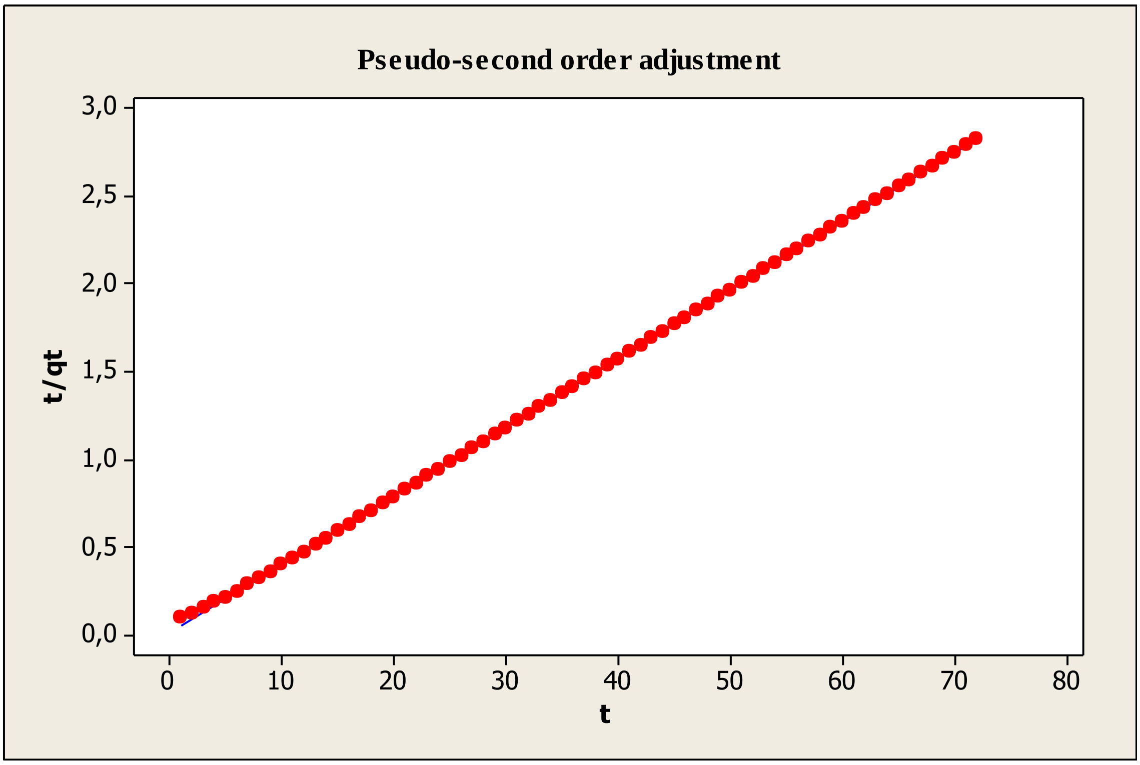

Figure 3.11

The ecuation function is `t/qt = 0,0118 + 0,0390*t` with a $R^2$of 1. Q_e value is equal to 26.64 and 1.662x10^{-5} is obtained for k_2.

4. Conclusions:

The activated carbon produced by physical activation shows acceptable capability of adsorption of 2,4-D and Cu. The equilibrium time takes several hours, this is good in continuous processes but in batch ones means that we are able to treat less amount of water and It could be a handicap in future industrial requirements.

The studies of surface area with BET analysis shows that the surface area obtained is directly proportional to the time and temperature of pyrolysis, decreasing again at high values due to the destruction of the micro pore structure.

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A. Appendix:

A.1 Ultraviolet/visible spectroscopy

A.1.1 Theory:

Visible light absorption is known to all of us, because this is what causes objects to be coloured. For example, a blue dye appears blue because the light at the red end of the spectrum is absorbed, leaving the blue light to be transmitted. The UV spectrometer used this property as base for its work.

Visible light lies in the wavelength range 4.0 – 7.0 x 10-7 m. To keep the numbers more manageable it is usually quoted in nanometres so that the range becomes 400–700 nm. When light is absorbed by a material, valence (outer) electrons are promoted from their normal (ground) states to higher energy (excited) states.

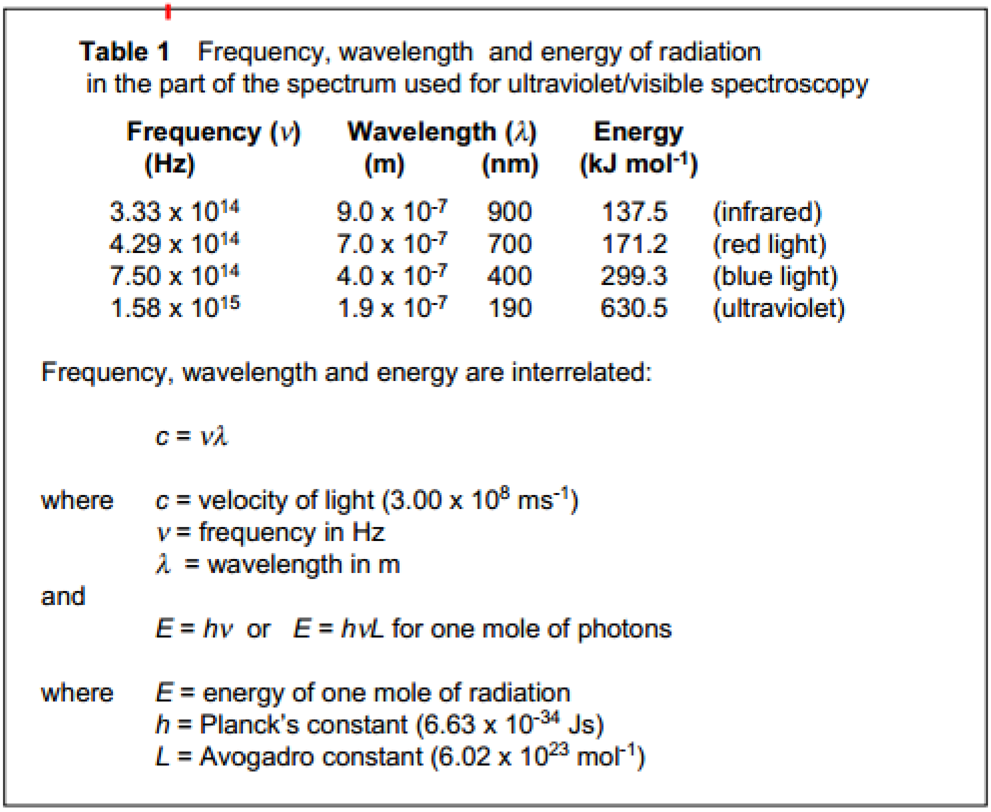


Table 1 Frequency, wavelength and energy of radiation in the part of the spectrum used for ultraviolet/visible spectroscopy

Frequency (ν)	**Wavelength (λ)**		**Energy**	
(Hz)	**(m)**	**(nm)**	**(kJ mol^{-1})**	
3.33×10^{14}	9.0×10^{-7}	900	137.5	(infrared)
4.29×10^{14}	7.0×10^{-7}	700	171.2	(red light)
7.50×10^{14}	4.0×10^{-7}	400	299.3	(blue light)
1.58×10^{15}	1.9×10^{-7}	190	630.5	(ultraviolet)

Frequency, wavelength and energy are interrelated:

$$c = \nu\lambda$$

where c = velocity of light (3.00×10^{8} ms^{-1})
ν = frequency in Hz
λ = wavelength in m

and

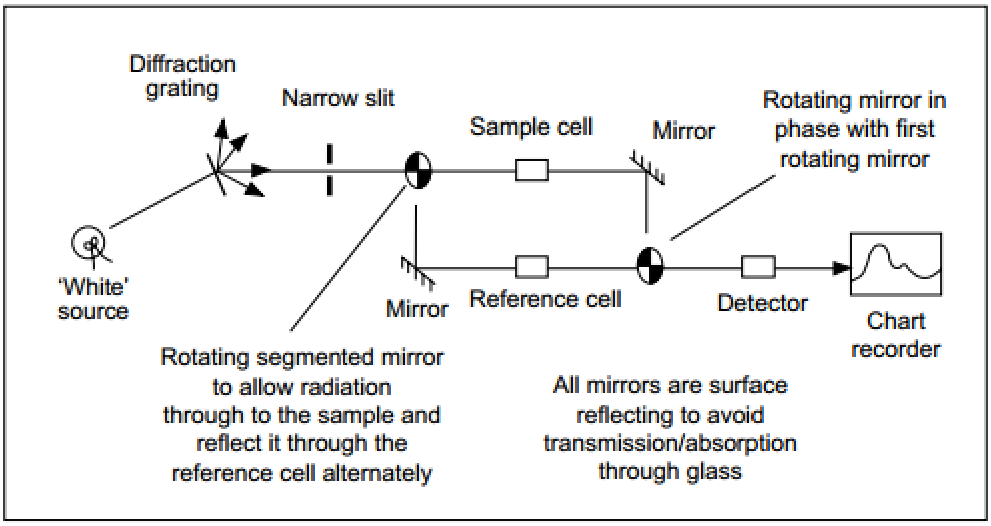
$$E = h\nu \quad \text{or} \quad E = h\nu L \text{ for one mole of photons}$$

where E = energy of one mole of radiation
h = Planck's constant (6.63×10^{-34} Js)
L = Avogadro constant (6.02×10^{23} mol^{-1})

The energy of visible light depends on its frequency. The promotion of electrons to different energy levels is not restricted to electromagnetic radiation in the visible part of the spectrum; it can also occur in the ultraviolet region. To encompass the majority of electron transitions the spectrum between 190 and 900 nm is usually considered.

A.1.2 The spectrometer (PG instruments LTD T80+) :

Because only small numbers of absorbing molecules are required, it is convenient to have the sample in solution (ideally the solvent should not absorb in the ultraviolet/ visible range however, this is rarely the case). In conventional spectrometers electromagnetic radiation is passed through the sample which is held in a small square-section cell (usually 1 cm wide internally). Radiation across the whole of the ultraviolet/visible range is scanned over a period of approximately 30 s, and radiation of the same frequency and intensity is simultaneously passed through a reference cell containing only the solvent. Photocells then detect the radiation transmitted and the spectrometer records the absorption by comparing the difference between the intensity of the radiation passing through the sample and the reference cells.



No single lamp provides radiation across the whole of the range required, so two are used. A hydrogen or deuterium discharge lamp covers the ultraviolet range, and a tungsten filament (usually a tungsten/halogen lamp) covers the visible range. The radiation is separated according to its frequency/wavelength by a diffraction grating followed by a narrow slit. The cells in the spectrometer must be made of pure silica for ultraviolet spectra because soda glass absorbs below 365 nm, and pyrex glass below 320 nm. Detection of the radiation passing through the sample or reference cell can be achieved by either a photomultiplier or a photodiode, that converts photons of radiation into tiny electrical currents; or a semiconducting cell (that emits electrons when radiation is incident on it) followed by an electron multiplier similar to those used in mass spectrometers. The spectrum is produced by comparing the currents generated by the sample and the reference beams. Modern instruments are self-calibrating, though the accuracy of the calibration can be checked if necessary. Wavelength checks are made by passing the sample beam through glass samples (containing holmium oxide) that have precise absorption peaks, and the absorption is calibrated by passing the sample beam through either a series of filters, each with a specific and known absorption, or a series of standard solutions.

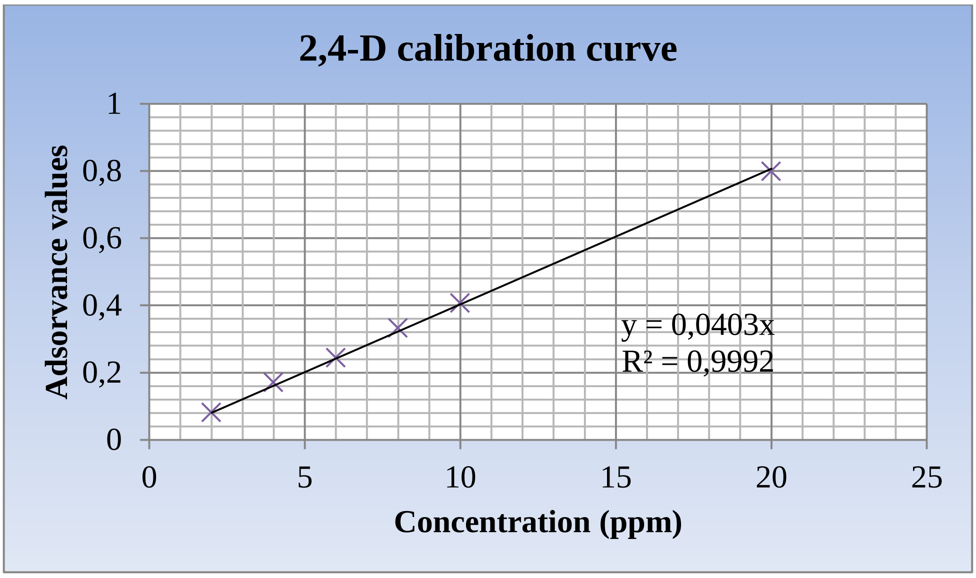
A.1.3 UV spectroscopy calibration curve for 2,4-D:

The UV spectroscope shows results according to and adsorvance value, but the device is not able to show this result in ppm units. Because of that with a serie of standard solutions a known concentration of 2,4-D can be related with an adsorbance value given by the spectroscope.

The standards solutions prepared according point 3.2 show the following adsorbance values:

C(ppm)	Adsorbance values
2	0,081
4	0,171
6	0,244
8	0,332
10	0,407
20	0,799

The literature says that a linear approach is the better way for relate this values with a equivalent real concentration of 2,4-D (appendix A.1). Plotting the results the calculations are showed at following graph:



The given ecuation shows a good accurate with an square R so close to one, that means that deviation of function from the real value according to standards points is negligible.

According to the ecuation, the analysis of samples after the adsorption studies will show an adsorbance value that will be 0.0403 times the real concentration of the sample.

A.2 Atomic absorption:

A.2.1 Atomic absorption theory:

Atomic absorption spectroscopy (AAS) has for many years been one of the chemist's favorite analytical tools for quantitatively measuring very small amounts (trace amounts) of metallic elements in samples as varied as alloys, rocks and soils, foods and drinks, surface waters, biological fluids, and reagent chemicals. Although the sensitivity of this technique varies somewhat from metallic element to metallic element as well as with the method of excitation (flame vs. graphite furnace for example), this technique is generally capable of accurately measuring a metallic element's concentration in a solution in the 1 to 100 ppm range (this is the reason because we diluited it by ten).. Because of its ability to measure the concentration of over 60 of the metallic elements at extremely low concentrations, atomic absorption spectroscopy has many, many analytical applications including impurity analysis of substances, forensic analysis, biomedical tissue, environmental samples and chemical research. Copper is important in the function of some enzymes. It is found naturally in extremely small amounts in some foods, milk for example. But it is frequently added to foods in small amounts.

The basic principle is that a solution (generally aqueous) containing the metallic element is aspirated in the form of an aerosol into a high temperature flame. The flame evaporates the solvent and decomposes the compound containing the element to create gaseous state atoms of the element. This technique is often called Flame Atomic Absorption Spectroscopy or "FAAS." Alternatively, an atomic vapor can be produced by rapid electrothermal heating of a graphite rod or tube on which a drop of the sample has been placed. This is accomplished using a "graphite furnace." This experiment uses an acetylene flame as the vaporization method.

A beam of monochromatic light with a wavelength at which only the element of interest can absorb, passes through the flame. The atoms of the element in the flame absorb some of the light. The amount of light absorbed is directly dependent upon the concentration of the element in the solution being vaporized in the flame. A beam of electromagnetic radiation characteristic of a particular element can be passed through the atomic vapor and monitored by a photomultiplier tube (PMT) detector. If the sample contains that particular element, its atoms will selectively absorb some of the electromagnetic radiation, thereby attenuating the beam and causing the detector signal to decrease.

This absorbance is proportional to the concentration of that element in the vapor and hence in the original sample.

There are many experimental variables in atomic absorption. Among them are:

(1) The quantity of material reaching the flame is dependent on 4 interrelated factors: (a) The rate of aspiration of the material into the flame, (b) the viscosity of the analyte solution, (c) the solvent, and (d) the surface tension of the analyte solution.

(2) The flame temperature is primarily determined by the choice of fuel and oxidant. Converse’s atomic absorption spectrometers are set up to operate on an acetylene/air mixture, hence this experimental variable is largely beyond our control with our systems.

(3) Furthermore, since the acetylene/air mixture is the most commonly used combination, we are not really hindered by our systems relative to most atomic absorption systems.

(4) The fuel/oxidant ratio affects the flame temperature to a more limited extent. More importantly, it determines whether the flame is a reducing or an oxidizing flame. Normally the reference literature tells you which type of flame is best for that analyte.

(5) There is also an optimum portion of the flame for analysis of the analyte. This variable is controlled by the burner height relative to the optical path. The optical path should be just above the tip of the inner blue cone of the flame. Another experimental consideration is the choice of calibration standards. The calibration standard should be in a matrix similar to that of the sample solution, For example, if sera are to be analyzed, then the standard solutions should be made to simulate serum. Ideally, if standards cannot be prepared in a matrix similar to that of the unknowns, then the technique of standard additions should be used. For most elements the range of analysis is between 1 and 50 ppm. Above the concentration of 50 ppm the absorbance is not linear relative to concentration for most elements. Each element has an optimum range within which the absorbance concentration relationship is linear (Beer’s Law).

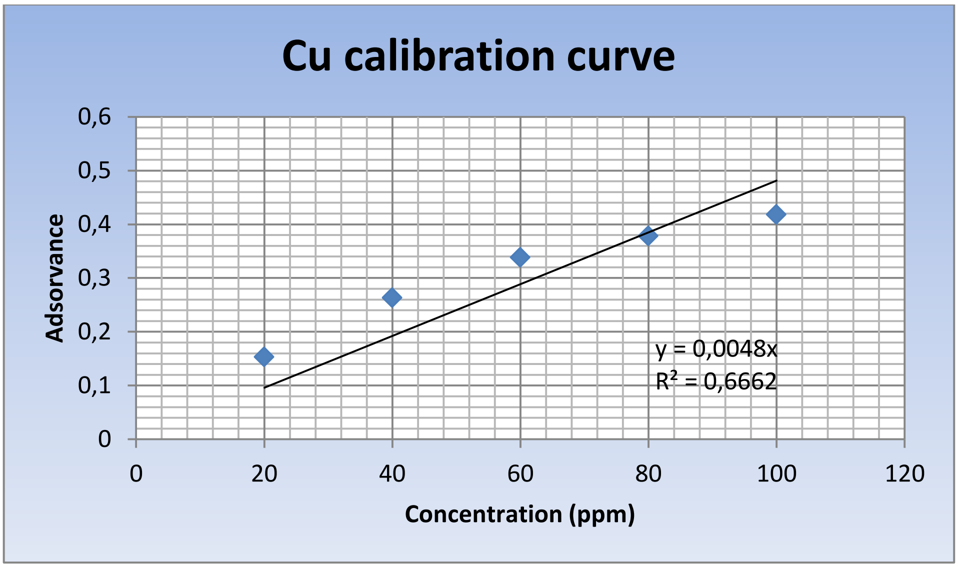
A.2.2 Atomic absorption calibration curve for Cu:

Atomic absorption device shows concentration values in a similar way that UV spectroscope, giving and absorbance value that should be compared with a standard solution serie for accurate the real value.

The analysis of the standards gave the results collected at the next table, that relate device values with known concentration values in ppm as previous calibration with 2,4-D.

C(ppm)	Adsorvance values
T(°C)	25
20	0,153
40	0,263
60	0,338
80	0,378
100	0,418

Again, for this calibration process, literature says that a linear approach is the better way for relate this values with real concentration, now focusing on Cu concentration in the samples (appendix A.2). Plotting the results the calculations are showed at following graph:



The approach shows and R square too low that means that the approach is not enough accurate. The copper concentration curve for atomic absorption is only linear at the beginning of the concentration range, but the entire approach should be considered as linear approach (appendix A.2). The concentration of copper in samples will be the absorbance value given by the device over 0.0048.

A.3 Kinetic models:

A.3.1 Pseudo-first order kinetic model:

The pseudo first-order equation (Lagergren, 1898) is generally expressed as follows: where q_e and q_t are the adsorption capacity at equilibrium and at time t, respectively (mg·g^{-1}), k_1 is the rate constant of pseudo first-order adsorption (l·min^{-1}).

$$\frac{dq_t}{dt} = k_1 (q_e - q_t)$$

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (3) becomes:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303} t$$

The values of $\log (q_e - q_t)$ were linearly correlated with t. The plot of $\log (q_e - q_t)$ vs. t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot, respectively.

A.3.2 Pseudo-second order kinetic model:

The pseudo second-order adsorption kinetic rate equation is expressed as (Ho et al., 2000) where:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \qquad \text{(eq.1)}$$

k_2 is the rate constant of pseudo second-order adsorption (g·mg$_{-1}$·min$_{-1}$).
For the boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of Eq. (1) becomes:

$$\frac{1}{(q_e - q_t)} = \frac{1}{q_e} + k\,t \qquad \text{(eq.2)}$$

which is the integrated rate law for a pseudo second-order reaction. Equation (2) can be rearranged to obtain Eq.(3), which has a linear form:

$$\left(\frac{t}{q_t}\right) = \frac{1}{k_2\, q_e^2} + \frac{1}{q_e}(t) \qquad \text{(eq.3)}$$

If the initial adsorption rate, *h* (mg·g^{-1}·min^{-1}) is:

$$h = k_2 q_e^2$$ (eq.4)

then Eqs. (3) and (4) become:

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e}(t)$$ (eq.5)

The plot of (t/q_t) and t of Eq. (3) should give a linear relationship from which q_e and k_2 can be determined from the slope and intercept of the plot, respectively.