



DETERMINATION OF URANINE ADSORPTION AND RECOVERY DEGREES FROM ACTIVATED CARBON BAGS - USED IN WATER ENVIRONMENT STUDIES

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ABSTRACT

The purpose of this paper relates to determining the adsorption and recovery degrees from activated carbon bags of Uranine (Fluoresceine) which can be used as fluorescent tracer in studies of aquatic environments. The effect of the activated carbon is that particles of the used dye are strongly fixed at the surface of the carbon grains. This attribute is used in different water systems studies with fluorescent tracer experiments. Carbon bags are used for the first time in our country in karst system study of Mali me Gropa. Adsorbed tracer (Uranine) can be extracted from carbon bags under the analytical procedures. Based on measurements of Uranine fluorescence intensity in standard solutions and extracts we can calculate its adsorption and recovery degree from activated carbon bags. The obtained results prove that extreme low traces of Uranine, which cannot be detected directly in the water sample, can be determined in carbon extracts.

Keywords: Artificial tracer, Fluorescence Intensity (I_F), Synchronous scan, Uranine, Activated carbon.

1. Introduction

The introduction of fluorescent tracers in hydrology has led to enormous methodological and instrumental developments. System's water is labelled through fluorescent dyes as artificial tracers and then their presence is monitored from time to time in various parts of the system

under the study. We can take this information measuring the dyes fluorescence intensity directly in water samples or in activated carbon bags extracts.

Granular activated carbon is a particularly good adsorbent medium due to its high surface area to volume ratio. One gram of a typical commercial activated carbon will have a surface area equivalent to 1,000 square meters. This high surface area permits the accumulation of a large number of contaminant molecules. The specific capacity of a granular activated carbon to adsorb organic compounds is related to: molecular surface attraction, the total surface area available per unit weight of carbon, and the concentration of contaminants in the wastewater stream (Shepherd, 1992).

Activated carbon is widely used for different purposes as good adsorbent in the removal of herbicide from water and other purposes (Bach et al. 2008; Snyder &...2001).

Synthetic organic compounds in water which include most of the herbicides are a major concern and cause of health risks in water supply systems. Advanced treatment processes such as powder activated carbon adsorption and granular activated carbon adsorption are effective in removing the herbicides (Areerachakul et al. 2007).

Some other results illustrate that granular activated carbon is an effective adsorbent for methyl *tert*-butyl ether and also provide specific guidance into adsorption of methyl *tert*-butyl ether on granular activated carbon in contaminated groundwater (Chen et al. 2010).

We will present in this paper some experiments about the ability of activated carbon to fix strongly Uranine at its grains surface. We have calculated the adsorption and recovery degree of Uranine from activated carbon bags used in Water System studies.

2. Materials and Methods

A container with grains of activated carbon is put into the water for one day or up to several weeks. The great advantage of this method is that springs or wells need not to be sampled continuously. Extreme low traces of dyes, which cannot be detected by spectrofluorometer directly from the water sample, can be determined in carbon extracts. The effect of the activated carbon is that traces of the used dye are strongly fixed at the surface of the carbon grains. They will not be washed out during a longer period of exposition. The dye will be enriched in the carbon and the measured concentrations of the dye in the extracts are 10 to 1000 times higher than average concentrations measured in the water samples of the same period. A disadvantage is that only qualitative results are available, because the exact concentration related to a certain

volume of water and the time when the dye has been adsorbed is unknown. Furthermore the upper limit of the adsorption capacity with regard to the natural background quality of the water is unknown too. So the results are normally given in scale units or relative intensity (Benischke, 1991; Käss, 1994).

We have used Uranine standard solution and active carbon bags (MERCK 2514) to determine the absorption and recovery of Uranine from carbon bags. The recovery of carbon active needs some special conditions (Areerachakul, N. et al. 2007).

Carbon bags recommended by Bauer (Fig. 1) contain an activated carbon with a grain size 1.5 mm (MERK, FRG No 2515). The material of the bag is nylon with a mesh width of 0.5-0.7 mm.

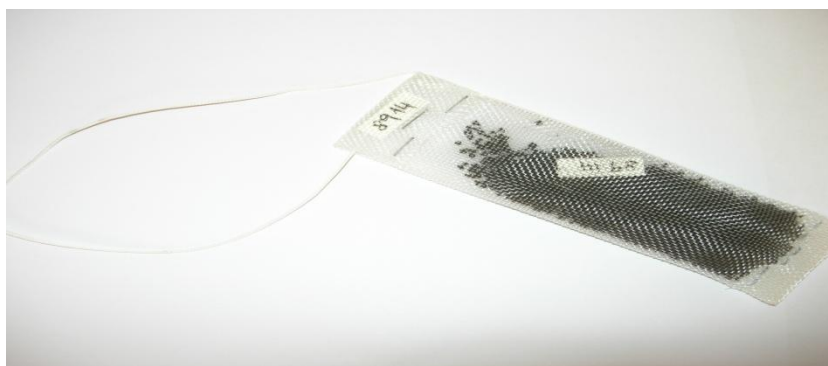


Fig. 1: Carbon bag (Bauer)

The exposition to the water should be such that the bag is fully immersed. One has to be sure that the water can flow through very well. After collecting them from the sampling points, we hang the bags on a cord for drying in the air for 1 or 2 days, in the laboratory.

Weighing of a quantity dried activated carbon was carried out by the means of an analytic balance (OHAUS Model GJ 610-2M) with 0.005 g reproducibility and ± 0.01 g linearity. The extraction of the dried activated carbon is carried out with a mixture that contains C_2H_5OH 96%: KOH 15% in 1:1 ratio in a glass test tube with a flat bottom and afterwards shaken in darkness for 1 to 2 hours in the shaker KIKA HS 501 digital. Finally the test-tubes are let in a dark compartment for another hour to allow all suspended material to fall down. (Käss, 1994; Kola, Amataj, 2006; Kola, 2008).

The concentration and synchronous scan methods were used for the measurement of Uranine fluorescence in standard samples and carbon bags extracts by the means of a Perkin Elmer Luminescence Spectrometer LS 55.

A special software package (FL WinLab) manages different application programs the instrument LS 55 offers. First the instrument stability is checked with regard to fluorescence intensity by the means of a reference material (Anthracene) (Perkin Elmer-1, 2000). The measurements validation with LS 55 instrument should be realized through Raman spectra (Raman Peak Wavelength, Raman Peak Intensity and Raman S/N ratio) from a sealed water cell (Perkin Elmer-2, 2000) and a reference material, Anthracene (Perkin Elmer-1, 2000). The method elaborated to measure Uranine fluorescence intensity is made up of the following parameters: Excitation wavelength- 491 nm; Emission wavelength- 512 nm; Ex. slit- 10.0 nm; Em. slit- 10.0 nm; $\Delta\lambda$ - 21 nm; etc. The instrument was previously calibrated with Uranine standard solutions by the means of the calibration application. Chemical treatment procedure has been applied for both samples and standards. We have previously analyzed some “blanks” in order to assess the natural presence of Uranine fluorescence, the so called “background”.

3. Results and Discussions

3. 1. Determination of Uranine adsorption degree from activated carbon bags

Determination of the degree of adsorption of Uranine from activated carbon bags, in our lab conditions, is described below.

It was prepared a Uranine standard solution and it was measured its fluorescence concentration $C_{0U} = 1.961$ ppb (by the means of a Perkin Elmer Luminescence Spectrometer LS 55). We took six sterile plastic bottles of 250 ml volume and were added in 100 ml standard solution of Uranine. In each of this bottle was introduced a carbon bag and the bottles were placed in horizontal position in the shaker. We controlled the carbon bags to be sure that they were completely immersed in the Uranine standard solutions. After that we applied different shaking time periods to each of the plastic bottle, namely 1 min, 4 min, 7 min, 10 min, 30 and 60 min. After that carbon bags were removed from bottles and hang them for drying. The respective solutions in six sterile plastic bottles were measured again for remained fluorescence of Uranine not adsorbed from active carbon bags - $C_{U\ Sol}$ (ppb) (Fig. 2).

These values were calculated in percentage, $C_{U\ Sol}$ (%), making reference to the concentration of Uranine standard solution ($C_{0U} = 1.961$ ppb).

Adsorption degree of Uranine A_U (%) from active carbon in different time is calculated from the formula:

$$A_U (\%) = \frac{C_{0U} - C_{U_{sol}}}{C_{0U}} 100$$

Where: C_{0U} – Uranine concentration in standard solution - 1.961 ppb

$C_{U_{sol}}$ - remained fluorescence of Uranine in solution, not adsorbed from active carbon (ppb).

Obtained results of Uranine concentrations remained in solution $C_{U_{sol}}$ (ppb and %) after being in contact with carbon bags for different shaking time periods are presented in table 1 and graphically in figure 2.

Uranine adsorption respective degrees (A_U %) from activated carbon are presented in table 1, too.

Tab. 1: Adsorption degree of Uranine (A_U) from activated carbon ($C_{0U} = 1.961$ ppb)

Nr. of carbon bag	Shaking time (minutes)	Uranine concentration in solution $C_{U_{sol}}$ (ppb)	$C_{U_{sol}}$ (%)	Adsorption degree. A_U (%)
1	1	0.222	11.32	88.68
2	4	0.131	6.68	93.32
3	7	0.093	4.74	95.26
4	10	0.064	3.26	96.74
5	30	0.055	2.78	97.22
6	60	0.041	2.09	97.91

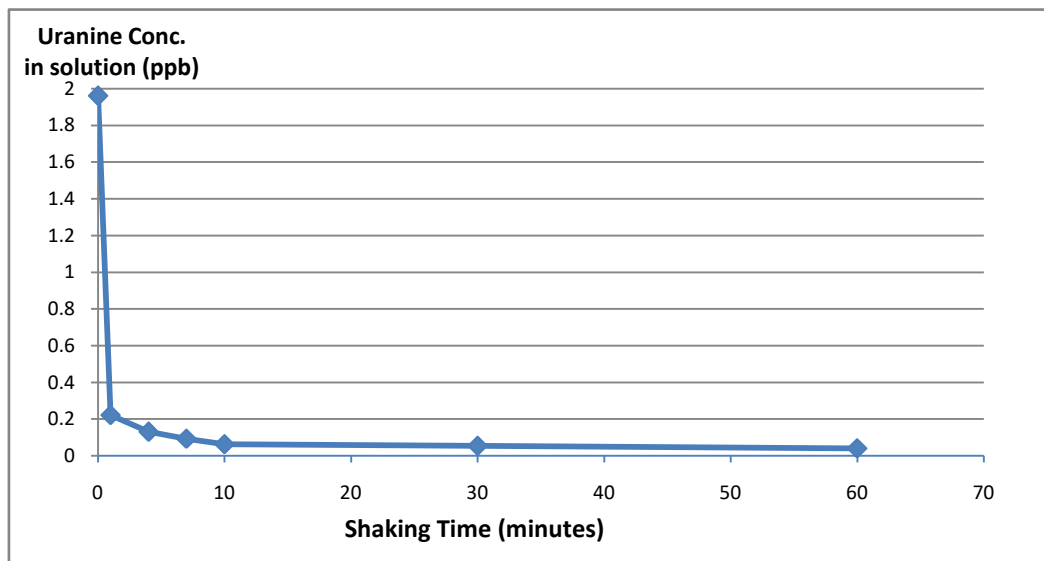


Fig. 2: Uranine concentrations in solution after being in contact with carbon bags for different shaking times

Dependence of Uranine adsorption degrees from the different shaking time periods is shown in figure 3.

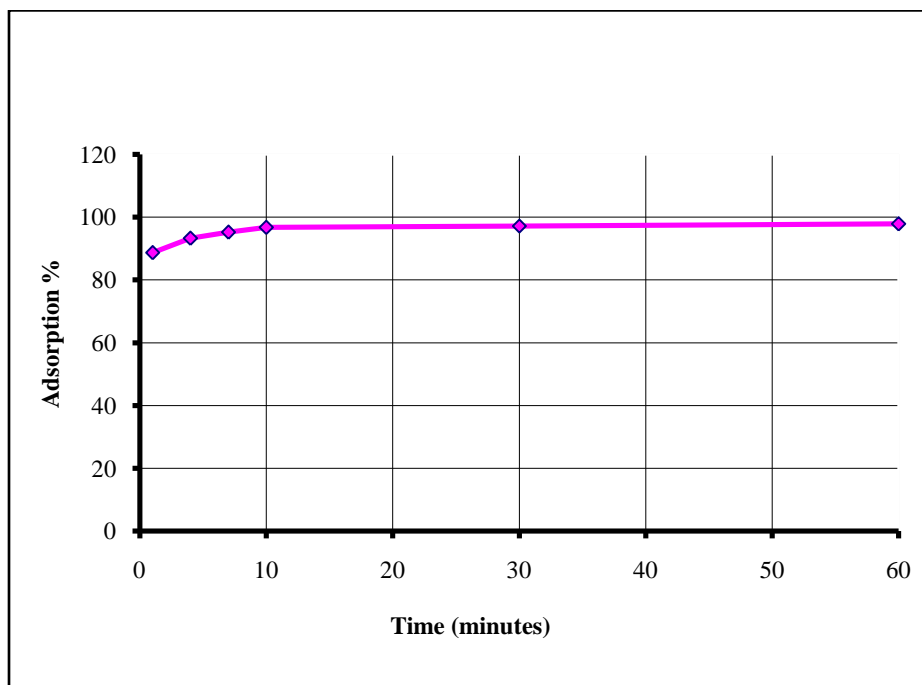


Fig. 3: Adsorption degree of Uranine (A_U) from activated carbon

This experiment showed that activated carbon adsorbed 88.68 % of Uranine just for one minute adsorption time and 97.91 % after 60 minutes. These results proved that Uranine was rapidly and strongly fixed at the surface of the activated carbon grains, so using the carbon bags in water system studies with Uranine, as artificial tracer, is helpful and convenient.

3. 2. Determination of Uranine recovery degree from activated carbon bags

According to our results, presented in table 2 and figure 4, the maximum extraction of Uranine from active carbon can be achieved by mixture 96% Ethanol, 15% KOH in the ratio 1: 1 (Kola, 2008).

Tab. 2: Uranine extraction from the same carbon bag with different mixture

Nr. of carbon bag	Mixture	Fluorescence Intensity	Concentration $C_{U\text{ extract}}$ (ppb)
8664 Kroi Isak 1	Distilled water	4.188	0.061
8664 Kroi Isak 2	Ethanol : KOH 50:50	447.422	6.466
8664 Kroi Isak 3	DMF : Dist. water 80:20	10.783	0.156
8664 Kroi Isak 4	Ethanol 96%	2.864	0.042

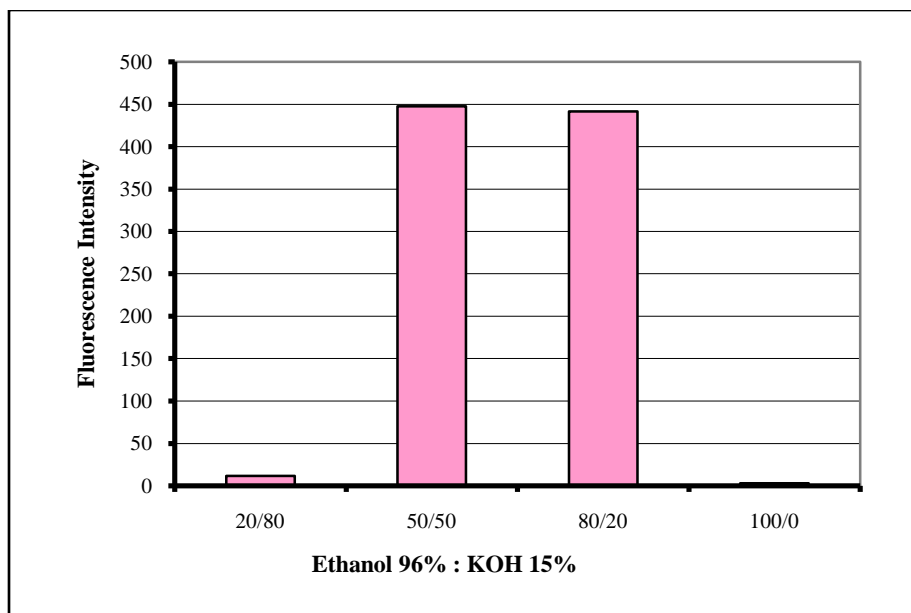


Fig. 4: Influence of the mixture ratio on Uranine fluorescence intensity

The maximum value of fluorescence Uraninës to extract mixing is achieved by extraction with 96% Ethanol, 15% KOH in the range of ratios from 50: 50 to 80: 20. Judging in terms of cost, we apply the ratio 50: 50.

Maximum emission values in general depend on the type of mixture ratio and extraction. In this case, Uranine fluorescence emission maximum can be shifted up to 520 nm (Käss, 1994).

Determination of the recovery degree of Uranine from activated carbon bags, in our lab conditions, is described shortly below.

We weighted 0.5gr carbon from dried carbon bags and extracted the Uranine from them with 7 ml mixture C₂H₅OH 96%: KOH 15% in 1:1 ratio.

The concentrations of Uranine were measured in obtained extracts (C_{UExt}) for different extraction time from one to 60 minutes.

The degree of recovery of Uranine (R_U) for each extraction time was calculated by comparing the amount of Uranine in extract (Q_{U Ext}) with its adsorbed amount from active carbon (Q_{U Ads}), expressed in percentage:

$$R_{RU} (\%) = \frac{Q_{UExt}}{Q_{UAds}} 100$$

After appropriate calculations the obtained values of the recovery degree of Uranine (R_U) from activated carbon for different extraction time are shown in table 3.

Tab. 3: Recovery degree of Uranine (R_U) from activated carbon ($C_{0U} = 1.961$ ppb)

Nr. of carbon bag	Extraction time (minutes)	$Q_{U\text{ Ext}}$	$Q_{U\text{ Ads}}$	Recovery degree R_U (%)
8674	1	0.03098	0.1739	17.82
8673	4	0.03791	0.183	20.71
8678	7	0.04064	0.1868	21.75
8677	10	0.04673	0.1897	24.63
8676	30	0.05334	0.1906	27.99
8675	60	0.0546	0.1917	28.44

Figure 5 shows the dependence of the degree of recovery of Uranine from the time of extraction from active carbon.

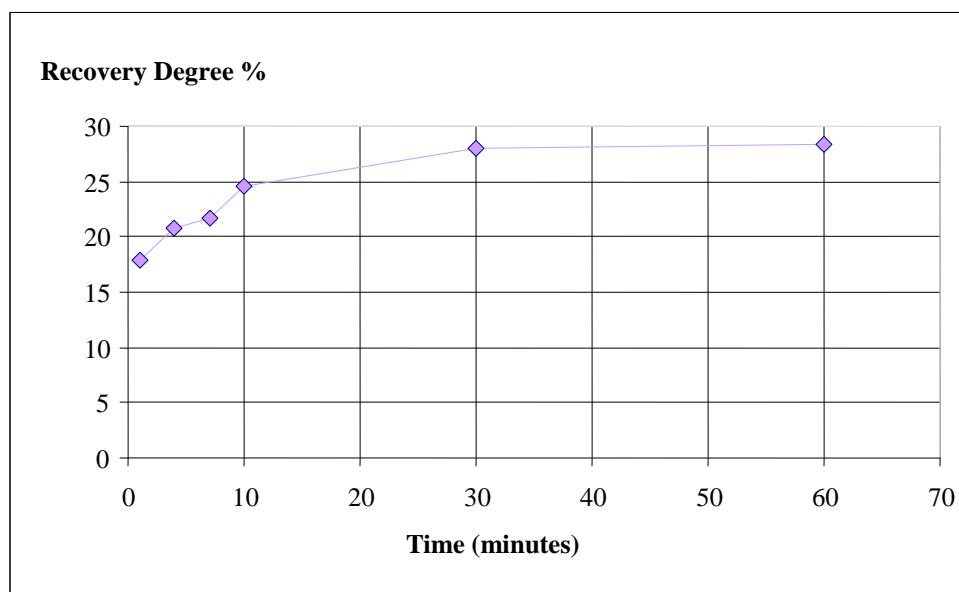


Fig. 5: Recovery degree of Uranine from activated carbon.

As seen from the results presented in the table 3 and in the figure 4, the degree of recovery of Uranine from active carbon varies from 17.82 % for one minute extraction, until 28.44 % for 60 minutes extraction time period.

4. Conclusions

According to our results the particles of the activated carbon adsorb 88.68 % of uranine just a minute after having been in contact with water containing tracer, so it seems clear that the carbon grains accumulate and fix very rapidly the fluorescent dye.

The degrees of recovery of uranine from active carbon are 17.82% to 28.44 % for the extraction time period from one to 60 minutes.

The obtained values of the recovery degrees of uranine from active carbon look to be small values but they are very significant if we consider that the measured concentrations of the dye in the extracts are 10 to 1000 times higher than average concentrations measured in the water samples of the same period.

The carbon bags can be used only to prove whether the dye has passed or not at sampling points where they are located, even when uranine was not detected in water samples from the same sampling point.

The obtained results prove that the use of the carbon bags in water system studies with fluorescent tracer is very helpful and convenient.

5. References

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Tables & Figures

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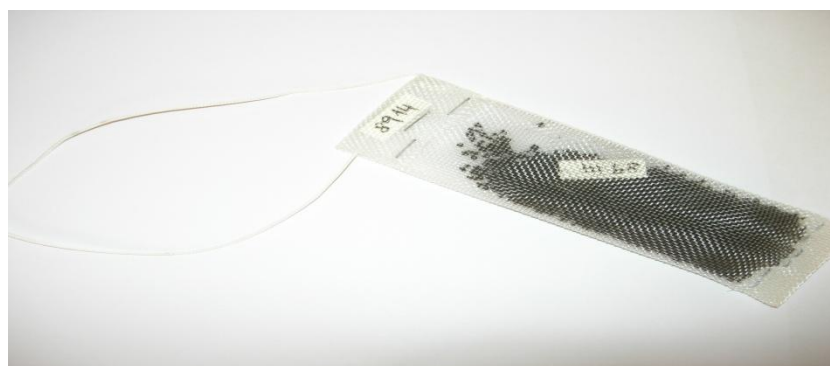


Fig. 1: Carbon bag (Bauer)

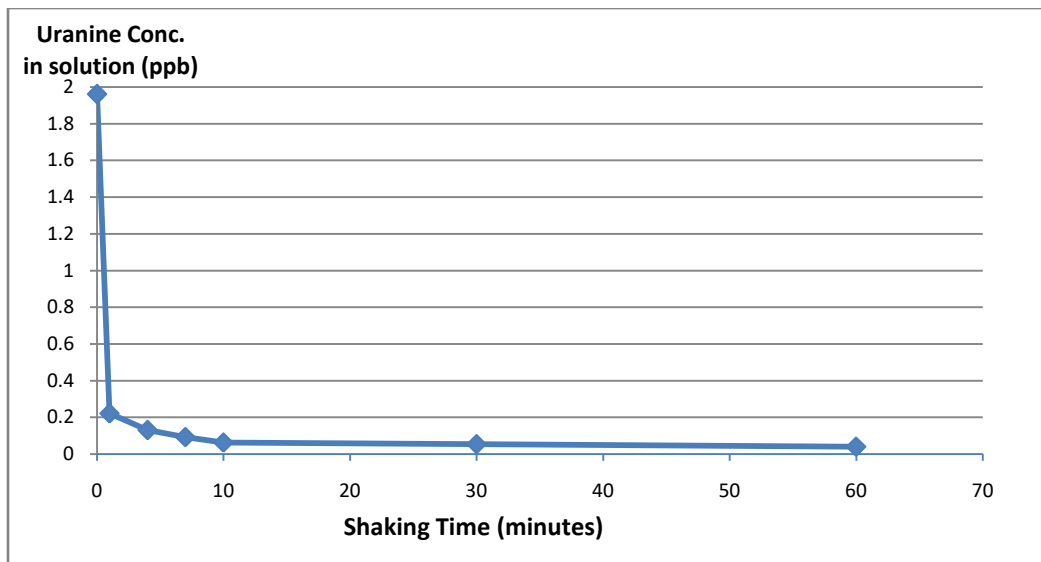


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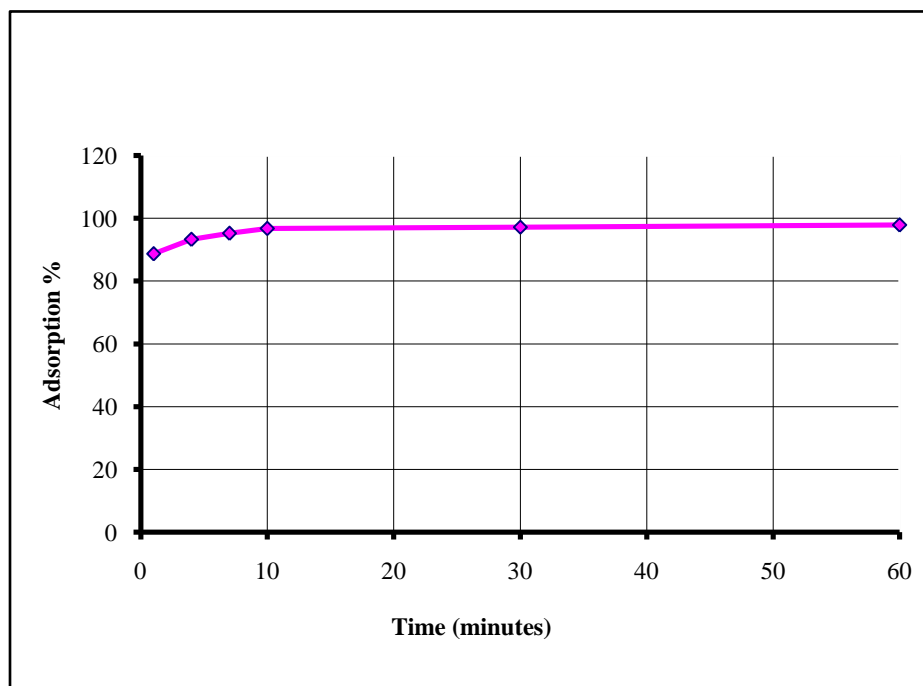


Fig. 3: Adsorption degree of Uranine (A_U) from activated carbon

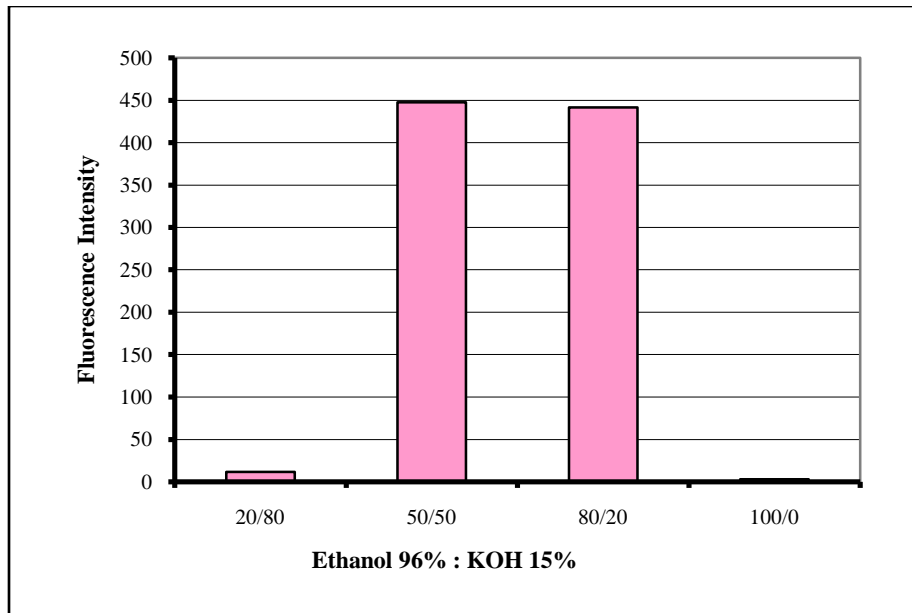


Fig. 4: Influence of the mixture ratio on Uranine fluorescence intensity

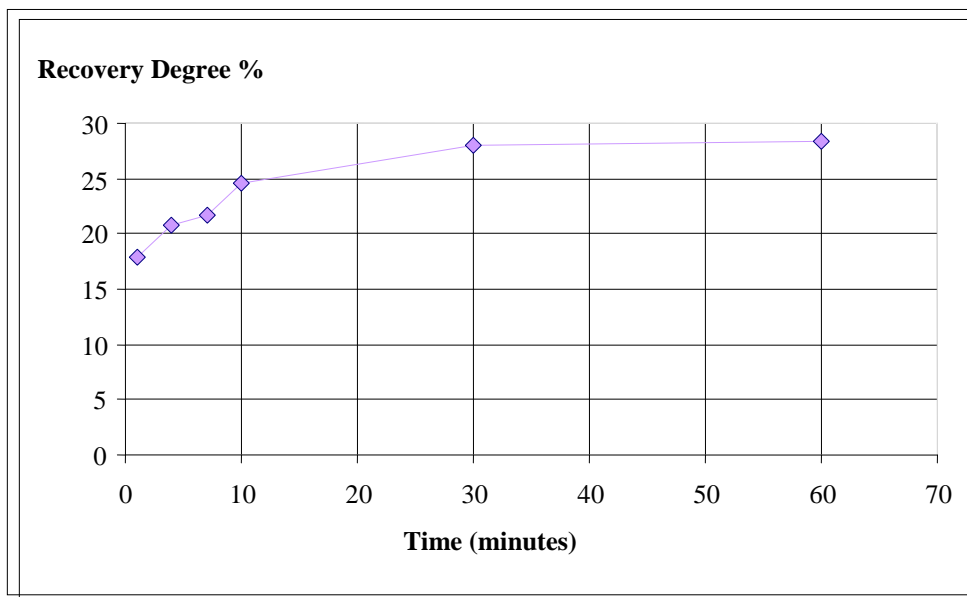


Fig. 5: Recovery degree of Uranine from activated carbon.