

*Article*

## COMPARATIVE STUDY CONCERNING THE REMOVAL OF PHENOL FROM WASTEWATER ON SLUDGE AND ZEOLITE\*

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### ABSTRACT

The present study presents two adsorbents which have been comparatively used in order to remove phenol from wastewater. Sludge from the wastewater treatment plant of Timisoara and zeolite of commercial origin are cheap and easily available materials. The adsorbent materials were characterized using the EDAX technique. The influence of the contact time and of the adsorbent mass was watched over the adsorption equilibrium and the optimal working conditions were settled regarding the phenol adsorption on these two materials.

**Keywords:** phenol, sludge, zeolite, adsorption

### 1. INTRODUCTION

Nowadays, a broad range of industries take benefit of phenol and its derivatives as raw materials, essentially serving for the production of different materials from plastics, epoxy resins or pesticides to pharmaceuticals [1]. On the other hand, when generated by the industries phenol and its derivatives are significant contaminants of wastewater [2-6].

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To living organisms phenol and its derivatives are highly toxic, harmful and corrosive being rapidly absorbed through the skin or following inhalation and ingestion. Once absorbed, the phenol and its derivatives are distributed throughout the body, concentrating mainly in the liver and kidneys.

In human body, phenol follows several stages of metabolism: conjugation, oxidation and excretion. The main mechanism consists of conjugation reactions (direct sulfation and glucuronidation) that result in the formation of glucuronide and sulfate ester. The phenol which is not directly conjugated may be the substrate for an oxidative metabolism, when its oxidation at dihydrodiols compounds occurs. These, in turn, can participate in conjugation reactions with the glucuronic acid and the sulfate. Through an enzymatic mechanism, the phenol and quinones such as reactive intermediates, in turn, are substrates for conjugation [7,8].

Regardless of the route of access into the body, phenol does not significantly accumulate in the body, being rapidly eliminated. The elimination occurs mostly through urine as sulfate and glucuronide conjugates. Therefore, direct conjugation of phenol and glucuronic acid or phenol and sulfate are the main mechanisms of detoxification, which represent the greatest part of phenol metabolism. [7].

According to the product Safety Data Sheet provided by some of the largest phenol producers such as SLOVNAFT VÚRUP [9], SIGMA-ALDRICH [10], AMRESCO [11], LIFE TECHNOLOGIES [12], AXIALL, LLC [13], SCIENCELAB.COM, INC. [14], CARLO ERBA REAGENTS [15], phenol presents:

- ✓ *acute dermal toxicity* (it is toxic in contact with skin, corrodes / irritate the skin; it causes severe skin burns, eye damage, even corneal perforation);
- ✓ *acute inhalation toxicity* (it is toxic if inhaled as vapour, it can lead to total intoxication damaging the CNS);
- ✓ *acute oral toxicity* (it is toxic if swallowed; it can lead to painful cauterization of the digestive tract and subsequent symptoms of damage to the CNS and can have lethal effects);
- ✓ *systemic toxicity over a target organ*- central nervous system, blood, liver, kidney (it can cause damage to organs through prolonged or repeated exposure);
- ✓ *susceptibility of causing genetic anomaly* (it is suspected of mutagenicity);
- ✓ *susceptibility of causing cancer*.

The particular high toxicity of phenol imposes a series of measures regarding its removal from various matrices. There are several methods for the removal of phenol from aqueous solutions, such as distillation, extraction, membrane processes, adsorption, chemical precipitation, ion exchange, reverse osmosis, chemical oxidation, solvent extraction / stripping gas, complexation, bioremediation.

Adsorption is an effective separation process, intensely studied and recently used for the treatment of industrial effluents and domestic wastewater.

A suitable adsorbent for wastewater treatment must possess a number of qualities [16]:

- ✓ to present a high affinity for the target compounds, translated into a high adsorption capacity;
- ✓ to ensure the greatest possible degree of removal from the wastewater of the targeted pollutant vector;
- ✓ to be stable and renewable;
- ✓ to allow desorption and recovery of the adsorbed compound;
- ✓ to have a low cost;
- ✓ to be tolerated by the environment.

Even though many adsorbents have been tested and reported in the literature, rarely they possess all of the characteristics mentioned above. This is the case for: activated carbon obtained in various ways [6, 17-22], activated carbon with various additions [23], ash and modified ash [24-29], hydroxyapatite [5, 30], polymeric resins or polymeric composites [31-33], alumina, silica gel, zeolite [34-37], chitin-chitosan [38-41], chitosan-alginate [42], modified bentonite and kaolinite [43], iron oxide [44]. Among them, natural and modified zeolites are of great importance [45-53].

For the present study two adsorbent materials have been used, sludge from Timisoara water treatment plant and zeolite of commercial origin, for the removal of phenol from wastewater. The aim was the comparative assessment of the performance of these two materials, which are quite affordable and can be easily procured.

## 2. METHODS AND MATERIALS

### *Adsorbent materials*

The sludge used for the adsorption study and phenol removal from aqueous solutions originates from the wastewater treatment plant "Stan Vidrighin" of Timisoara.

The sludge was dried in an oven at 95°C for 12 hours, after which it was ground and sieved through a metallic sieve.

The zeolite used as adsorbent material comes from the CEO EcoNatura Company, Romania. Mineralized zeolitic volcanic tuff has been obtained from volcanic rocks rich in natural zeolite, in which clinoptilolite is predominant.

### *Reagents and Solutions*

The following reagents were used: phenol (Fluka), 4-amino-antipyrine (Sigma-Aldrich), hexacyanoferrate (III) (Fluka), 25% ammonia (Sigma-Aldrich), ammonium chloride (Sigma-Aldrich), chloroform (Sigma-Aldrich), double distilled water.

All reagents were of analytical purity.

The stock solution of phenol, with a concentration of 1 g/L, was obtained by dissolving the appropriate amount of phenol, weighed to an accuracy of  $\pm 0.0001$  mg, in double distilled water, in a volumetric flask.

Phenol standard solutions, of various concentrations, were prepared by serial dilutions of the stock solution with double distilled water.

### *Instruments and devices*

For the adsorption experiments, it was used a thermostated shaker type Vibramax 100 Heidolph whose stirring rate was set at a constant value of 200 rpm.

The phenol concentration from the initial sample and from the one subjected to the absorption was determined spectrophotometrically according to the method ISO 6439:2001 with the aid of a T90 UV / VIS dual beam spectrophotometer type, PG Instruments Ltd. The working wavelength was 460 nm, using a 1cm quartz cuvette.

### *Working methodology*

The measurements were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ), without pH adjustment of the solutions.

For each adsorption experiment, the appropriate amount of adsorbent material was added to 50.0 mL of phenol solution in a 100 mL beaker. The samples were shook at a constant speed (300 rpm) for 15, 30, 45, 60, 90, 120 and 150 minutes.

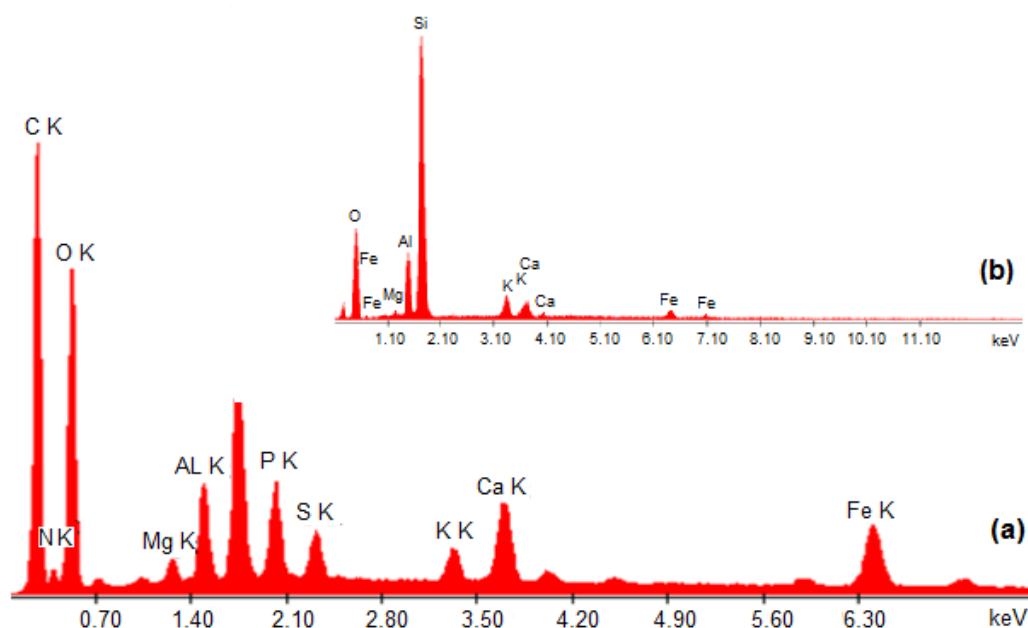
After the time in contact, samples were filtered with a vacuum pump and the filtrate was used for the spectrophotometric determination of the residual phenol.

### 3. RESULTS AND DISCUSSIONS

#### *Characterization of the adsorbent materials*

The morphology of the adsorbents surface was characterized by energy dispersive X-ray analysis (EDAX). EDAX studies of the dry sludge and zeolite samples were performed using an electron microscope FEI Inspect S.

**Figure 1:** EDAX spectra for (a) sludge and (b) zeolite



In Figure 1 (a) and (b) are given the EDAX spectra for dried sludge and zeolite. Table 1 presents the elemental composition of the dried sludge.

In the case of dry sludge, EDAX spectra indicate the presence of metals such as Al - 2.50%, Fe - 2.00% Ca - 1.24%, Mg - 0.60%, K - 0.46%, along with other elements such as N - 6.09% Si - 3.90%, P - 1.52% and S - 0.608%. As expected, best represented elements are C - 51.06% and O - 30.39%, which indicate the presence of organic matter and water.

For comparison, the EDAX data from Figure 1 (b) are presented revealing the main elements in zeolite: Si, Al and O, as confirmation for zeolite as an aluminosilicate. Beside these elements, zeolite contains much smaller amounts of K, Ca, Mg and Fe. The EDAX data also indicate that the Si/Al ratio is approximately 4.5. In the specialized literature Si/Al

reports are indicated ranging from 4.0 to 5.3 corresponding to chemical composition of pure clinoptilolite. On the other hand, heulandite, another zeolitic mineral with a similar structure of clinoptilolite has a Si/Al ratio of 2.7 [16, 54, 55]. EDAX data therefore prove that zeolite used for this specific study as adsorbent material has the basic structure of clinoptilolite type.

**Table 1:** Elemental composition of dry sludge

EDAX ZAF Quantification (Standardless)						
Element Normalized						
SEC Table : Default						
Element	Wt %	At %	K-Ratio	Z	A	F
C K	51.06	60.95	0.1706	1.0136	0.3296	1.0003
N K	6.09	6.24	0.0064	1.0061	0.1041	1.0006
O K	30.39	27.24	0.0431	0.9994	0.1420	1.0001
MgK	0.60	0.36	0.0019	0.9637	0.3332	1.0021
AlK	2.05	1.09	0.0088	0.9364	0.4565	1.0029
SiK	3.90	1.99	0.0215	0.9648	0.5698	1.0018
P K	1.52	0.70	0.0090	0.9338	0.6334	1.0014
S K	0.68	0.30	0.0048	0.9590	0.7346	1.0014
K K	0.46	0.17	0.0042	0.9098	0.9852	1.0050
CaK	1.24	0.45	0.0118	0.9312	1.0191	1.0022
FeK	2.00	0.51	0.0184	0.8635	1.0674	1.0000
Total	100.00	100.00				

#### ***Optimal conditions of work. Influence of contact time***

In order to study the influence of the contact time, samples of a given concentration of phenol were stirred together with different amounts of adsorbent at certain periods of time: 15, 30, 60, 90, 120 and 150 minutes in case of zeolite and 15, 20, 30, 60, 90 and 120 minutes in case of sludge. The yield variation and the adsorption capacity variation with contact time have been observed. Reaching the plateau region corresponds to the establishment of the adsorption equilibrium.

The plots  $\eta$  [%] =  $f(t)$  and  $q_e = f(t)$  for the adsorption of phenol on zeolite, are given in Figure 2 (a) and (b), and for the adsorption of phenol on sludge in Figure 3 (a) and (b).

When adsorption is performed onto sludge, Figure 2 (a) and (b) shows that, for the initial concentration of phenol of 1 mg/L (1 ppm), the highest adsorption occurs within the first 30 minutes, after which the adsorption yields and the adsorption capacity increase further tending towards an equilibrium that is reached after 60 minutes.

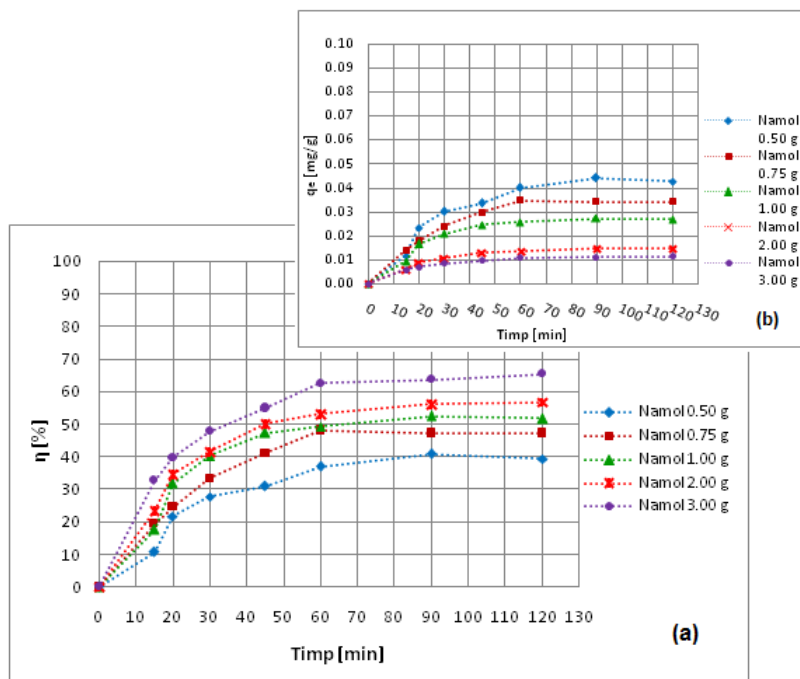
In this phase, we can assert that the removal of phenol from solution ceases. Only one exception: for 0.50 g of sludge the adsorption equilibrium is reached after 90 minutes. Therefore we chose the *optimal contact time on sludge of 90 minutes*.

Depending on the amount of sludge, adsorption yield is between 39.35% (on 0.50 g sludge) and 65.44% (on 3.00 g sludge).

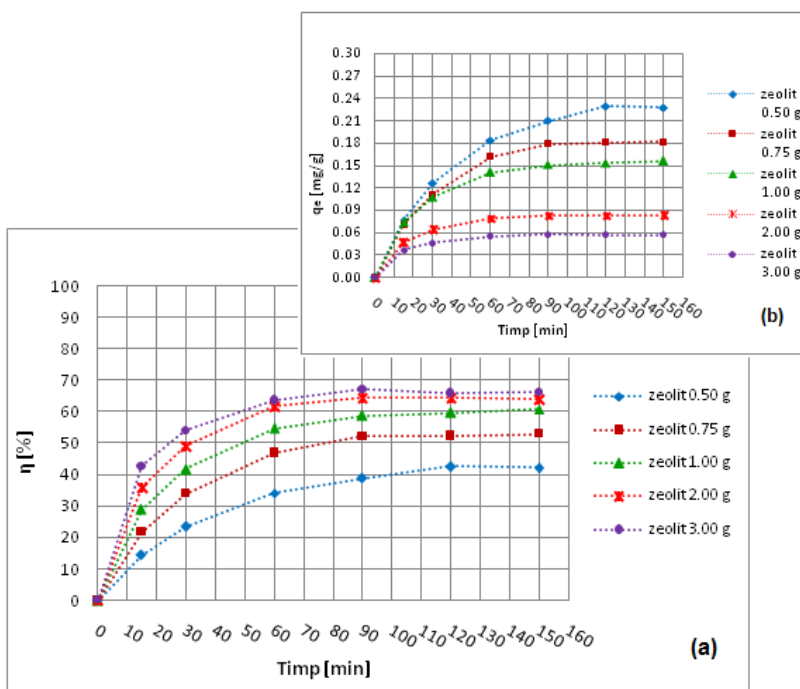
The adsorption onto zeolite reveals the plateau, for the same initial concentration of phenol of 1 mg/L (1 ppm), after 90 minutes (Figure 3 (a) and (b)). In this case, the exception comes for 0.50 g of zeolite, where the adsorption equilibrium is reached after 120 minutes of contact. To be on the safe side, the *optimal contact time on zeolite* was chosen at *120 minutes*.

The range in which adsorption yield is comprised also depends on the amount of adsorbent: between 42.13% (per 0.50 g zeolite) and 66.12% (by 3.00 g zeolite).

**Figure 2:** (a)  $\eta$  [%] =  $f(t)$  and (b)  $q_e$  [mg/g] =  $f(t)$ , at phenol adsorption on sludge;  $C_{i\text{Ph}} = 1$  mg/L (1 ppm)



**Figure 3:** (a)  $\eta$  [%] =  $f(t)$  and (b)  $q_e$  [mg/g] =  $f(t)$ , at phenol adsorption on zeolite;  $C_{i\text{Ph}} = 1$  mg/L (1 ppm)



**Optimal conditions of work. The influence of adsorbent mass**

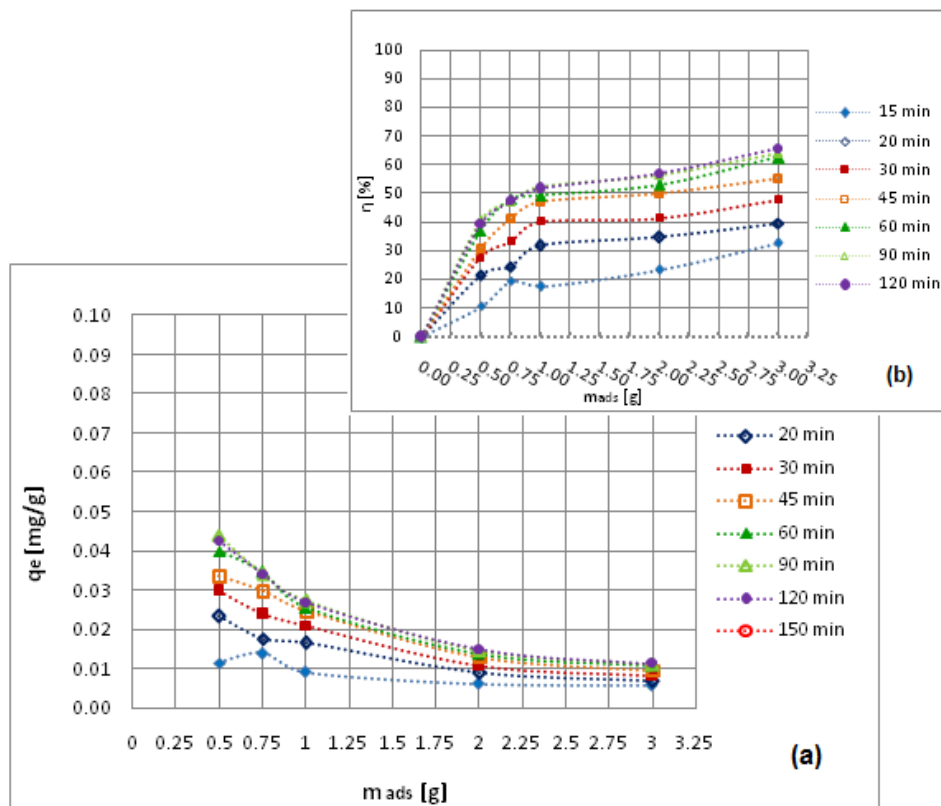
To determine the influence the mass of adsorbent brings, the phenol samples were placed in contact with 0.50; 0.75; 1.00; 2.00 and 3.00 g of each adsorbent, between 15 and 150 minutes. The variation of the yield and of the adsorption capacity with adsorbent mass has been recorded. The obtained plateau region corresponds to the establishment of the adsorption equilibrium.

The plots  $\eta$  [%] =  $f(m_{ads})$  and  $q_e = f(m_{ads})$  for the adsorption of phenol on both adsorbents are given in Figures 4 (a) and (b) and 5 (a) and (b).

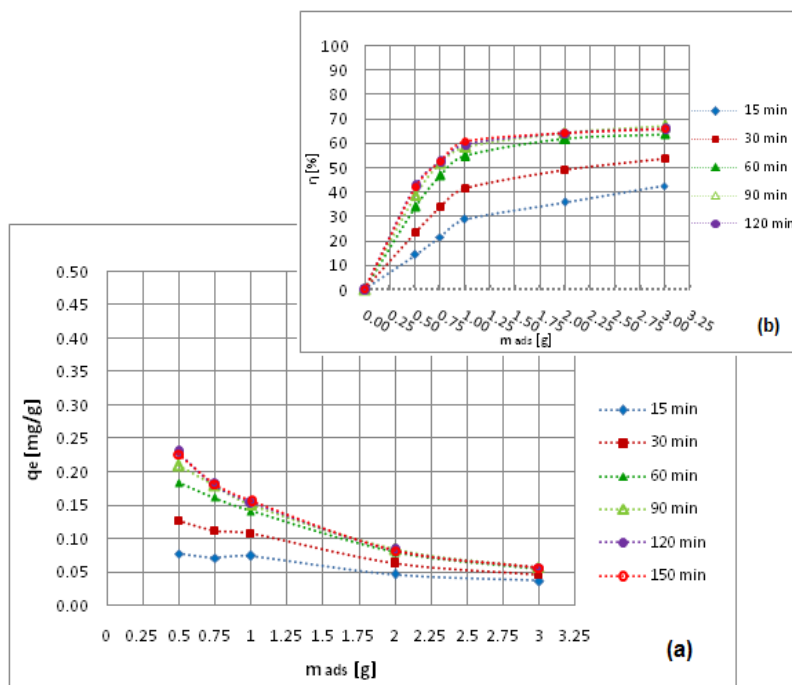
In case of sludge (Figure 4 (a) and 4(b)) the adsorption equilibrium is reached for an amount greater than 2.00 g of adsorbent. In this case, it was considered that for a phenol solution of 1 ppm, the optimum mass of adsorbent is 2.00 g.

Figure 5 (a) and (b) indicate that phenol adsorption onto zeolite reaches the equilibrium also for quantities larger than 2.00 g of adsorbent. This value was considered the optimum mass of zeolite for 1 ppm phenol adsorption.

**Figure 4:** (a)  $q_e$  [mg/g] =  $f(t)$  and (b)  $\eta$  [%] =  $f(t)$ , at phenol adsorption onto sludge;  $C_{iPh} = 1$  mg/L (1 ppm)



**Figure 5:** (a)  $q_e$  [mg/g] =  $f(t)$  and (b)  $\eta$  [%] =  $f(t)$ , at phenol adsorption onto zeolite;  $C_{i\text{ph}} = 1$  mg/L (1 ppm)



#### 4. CONCLUSION(S)

There have been studied and established optimal working conditions for the phenol adsorption from solutions with an initial concentration of 1 ppm, on zeolite and on sludge.

It has been found that, at room temperature, the most favorable working conditions for the adsorption of phenol from a solution with a concentration of 1 mg / L, are:

- on zeolite: 120 minutes contact time and 2.00 g adsorbent / 50 mL sample;
- on sludge: 90 minutes contact time and 2.00 g adsorbent / 50 ml sample.

In terms of contact time, the sludge is more indicated as adsorption material, having a faster adsorption time.

In terms of performance, under optimal working conditions (the ones mentioned above), the yield of adsorption is slightly better on zeolite than on sludge. But not also the adsorption capacity, which is net superior in case of the zeolite:

- zeolite: 64.28% adsorption efficiency and 0.083 mg /g adsorption capacity;
- sludge: 56.27% adsorption efficiency and 0.015 mg /g adsorption capacity.

The studies have shown an increase of the adsorption efficiency of phenol, as well as the contact time increased, as also at a weight increase of the adsorbent. This was due to the fact that the number of adsorption sites increased, at the increase of the adsorbent dose [5, 16]. A further increase of the contact time or of the adsorbent dosage over the optimal value is unjustified, the increase of these parameters becoming in this case insignificant, suggesting an evolution towards a plateau, a balance zone. The explanation is, that in time, the amount of



active sites decreases, the adsorbent becoming more agglomerate, thus hindering the free movement of its inner particles [4, 16].

On the other hand, the value of the adsorption capacity is high at low doses and reduced at high doses of adsorbent. Therefore, in accordance with the literature data [5, 56], has been noticed a decrease of the adsorption capacity, at an increase of the adsorbent quantity. This seems obvious, if we consider the mood of defining and of calculus, of the adsorption capacity. At the increase of the adsorbent mass, the quantity absorbed per its unit mass remains constant and the number of active sites remained the same. The number of mass units grows faster, in comparison to the amount adsorbed on them, which has as result a decrease of the adsorption capacity value. Transposed on the adsorption mechanism, the explanation of this conduct must consider several factors. The Langmuir approach of the adsorption, according to which the saturation is reached at the adsorbent surface coating with a monolayer of adsorbed molecules, may explain why the amount adsorbed per mass unit does not increase proportionally to the one absorbed on the entire adsorbent mass. However, the finding that the increase of adsorption is not commensurable with an increase of the adsorbent dose, suggests that there are a number of adsorption sites, which remain unsaturated during the adsorption, which leads to a lower use of the adsorption capacity of the adsorbent [5, 16].

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