

Removal of Phenols from the Water Effluents of Olive Presses

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Abstract – The water effluents of olive presses contain a number of phenols that are hardly biodegradable and therefore constitute an environmental hazard, mainly in the Mediterranean countries. The present work presents the results obtained from the study of artificial solutions containing one kind of phenol, namely gallic acid that consists of the main type of phenols present.

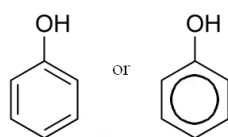
According to the experimental procedure, the phenol is removed from the water solution by absorption on different naturally occurring raw rock materials. The first material is caustic magnesia produced after the calcination of a magnesite sample from Macedonia, Greece, the second is a sample of sedimentary psammitic marl from the area of Chania, Crete, Greece, and the third solid absorbent is a bentonite sample from the island of Milos, Greece.

According to the results obtained, magnesia seems to be by far the best absorbent, with an absorbing capacity of 3500 mg of phenol per gram, followed by the psammitic marl. The absorbing capacity of bentonite is almost negligible.

Keywords – absorption of phenols, olive presses water effluents, magnesia, psammitic marl, bentonite

I. INTRODUCTION

Phenols are organic compounds consisting of a hydroxyl group directly bonded to an aromatic hydrocarbon group. The simplest of the class is C_6H_5OH , [1].



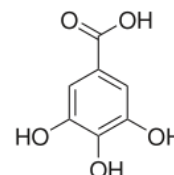
Although phenols have the hydroxyl group their structure, with the aromatic ring, gives them unique properties with acidity which is between that of aliphatic alcohols and carboxylic acids [1]. Phenols constitute a widespread and important class of water pollutants and are considered as priority of pollutants due to their antimicrobial and phytotoxic characteristics [2]. They are released into the environment in a number of different ways, as a byproduct of industrial and agro-industrial activities, such as chemical, paper and wood industry, metallurgy and cocking plants, as well as olive oil production, tomato processing, and wine distilleries. Phenols are also introduced in the environment by diffuse emissions including tar used to coat roads and pipes and some pesticides as well as their transformation products [3].

The water effluents of olive presses, (also called *katsigaros* in Greek) contain very high amounts of organic matter (up to 15% by weight), are resistant to degradation and constitute an important environmental problem due to the content of phenolic compounds. In fact, 2.5 litres of waste are released per litre of oil produced and 1.4 million m^3 of water effluents are produced every year in Greece alone and a total of 30 million m^3 are produced in the Mediterranean area [4,5]. It is important to remove phenols and aromatic compounds from contaminated industrial aqueous streams before they are discharged into any water reservoir. The conventional techniques used to remove phenol compounds include absorption, extraction, steam distillation, bacterial, chemical, and irradiation techniques [6].

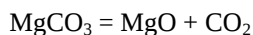
Literature survey [2-8] shows that absorption processes appear to be the treatment of choice since it can be applied to effectively remove different types of phenols in a simple and economical way. A large number of alternative, environmental friendly, absorbents of low cost have been studied. Such absorbents are industrial and agricultural wastes, different types of biomass, as well as some natural resource materials such as clay minerals, fly ash, spent bleaching earth, apricot stone shells, waste tire rubber, etc. have been utilized for this purpose [2,7,8].

II. MATERIALS AND METHODS

For the purpose of the present work, a synthetic phenol solution was used made of gallic acid dissolved in water at an initial concentration of 1.5 g/litre. Gallic acid is a type of phenolic acid also known as 3,4,5-trihydroxybenzoic acid and, despite its name, it does not contain gallium. The chemical formula is $C_6H_2(OH)_3COOH$ and its structural form is shown below, [1].



The absorbents used in the present work are caustic magnesia, psammitic marl and bentonite. Caustic magnesia (MgO) is the calcination product of magnesite ($MgCO_3$) that decomposes according to the following reaction at 1000 °C.



The magnesia produced at 1000 °C is active and has many applications in environmental applications due to its basic reaction in water. The sample used was a powder minus 53 µm provided by Grecian Magnesite S.A., a mining company in Macedonia, Greece.

The psammitic marl sample was collected from a natural sedimentary rock in the district of Chania on the island of Crete, Greece. After drying, the sample was crushed in a laboratory jaw crusher to minus 4mm. The crushed product was added in water and agitated for an hour until it was dispersed in the water. The pulp was then screened on a 53 µm screen and the minus -53 µm fraction, about 85% of the initial weight, was used for the absorption tests after filtration and drying.

The bentonite sample, in the form of a powder minus 53 µm in size, originated from the island of Milos in the Aegean Sea, Greece and provided by Akrolithos S.A., a mineral processing company operating in Rethymnon, Crete.

The surface area of the materials used as absorbents was measured by the B.E.T. nitrogen absorption method and the results obtained are presented in Table I. Magnesia has the largest specific surface area of all three materials.

TABLE I
SPECIFIC SURFACE AREA OF THE SAMPLES

Sample	S.S.A. (m ² /gr)
Magnesia	52.98
Psammitic marl	13.53
Bentonite	23.10

The chemical composition of the absorbents was determined by the x-ray fluorescence (XRF) method and the results are presented in Table II.

The semi-quantitative mineralogical composition of the samples was determined by X-ray diffraction (XRD) and is presented in Table III.

For all the absorption tests, 1 litre of water solution containing 1500 mg of gallic acid was used, having an initial pH=4. Two different series of tests were performed. In the first series of tests at time zero a predetermined quantity of the absorbent tested was added to the solution and the pulp formed was agitated with a magnetic stirrer. At predetermined time intervals, the pH was measured and a 15 ml sample of the pulp was taken, centrifuged to separate the solids from the liquid phase and forwarded for phenol concentration analysis. No more solids were added during the test.

For the second series of tests at each time interval, after measuring the pH and taking the sample for phenol analysis, an equal quantity of the solid absorbent under investigation was added to the pulp. This is repeated until the total predetermined quantity of the absorbent was added.

TABLE II
CHEMICAL ANALYSIS OF THE THREE SAMPLES WT %

Element	Magnesia	Psammitic marl	Bentonite
CaO	3.2	36.4	6.1
SiO ₂	4.5	25.9	49.4
Na ₂ O		4.6	
Fe ₂ O ₃	0.3	4.0	6.4
Al ₂ O ₃		3.3	11.5
MgO	88.1	2.3	3.0
K ₂ O		1.2	
SO ₃	0.4		1.8
TiO ₂			1.2
LOI	3.0	25.5	19.6

TABLE III
SEMI QUANTITATIVE MINERALOGICAL ANALYSIS

Mineral	Magnesia	Psammitic marl	Bentonite
Smectite			85
Quartz	4.5	40	7
Calcite	3.5	54	8
Mica		3	
Chlorite		3	
Dolomite	4		
Lime	3		
Periclase	85		

The concentration of water soluble phenols was determined with the spectrophotometric, Folin–Ciocalteu method [9] using gallic acid as standard. Aliquots of the samples containing up to 10 mg/l phenols were mixed thoroughly with 0.2 ml of Folin–Ciocalteu reagent in 10mL volumetric flasks. After 3 minutes, 1 ml of 35% w/v Na₂CO₃ was added and made to volume with deionized water. The samples were agitated and left for 60 min to stand at room temperature. Subsequently, the absorbance at 725nm was measured using a DR/400U (HACH) spectrophotometer. A five point calibration curve was prepared using gallic acid solutions (1-10 mg/l). The measurements were carried out in duplicates and all reagents used were of analytical quality.

III. RESULTS

A. Series 1: Direct addition

In this series of tests a predetermined quantity of the absorbent tested was added to the solution at time zero and no further additions of the absorbent were made.

Magnesia

The results of phenol absorption on magnesia are presented in Figures 1 to 4 for three levels of magnesia addition namely 5, 1 and 0.2 g per liter of solution. Figure 1 presents the

concentration of the remaining phenol in the solution as a function of time. At the beginning phenol is reduced rapidly and the rate of reduction is slowed down as time passes. The reduction is greater for larger amounts of the magnesia used.

Figure 2 presents the amount of phenol absorbed per gram of magnesia added. It is clear from this figure that the amount of phenol absorbed per gram of magnesia is greater for small quantities of magnesia used. It is important to compare the amount of phenol available per gram of magnesia added to the maximum amount absorbed per gram of magnesia. This is done in Figure 3 where it is obvious that at large amounts of magnesia added, almost all the available phenol is absorbed and there is no phenol available for further absorption.

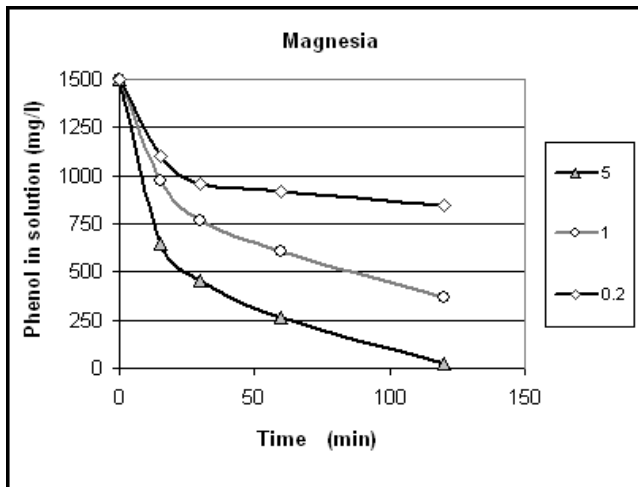


Fig. 1. Remaining phenol (mg/l) in solution.

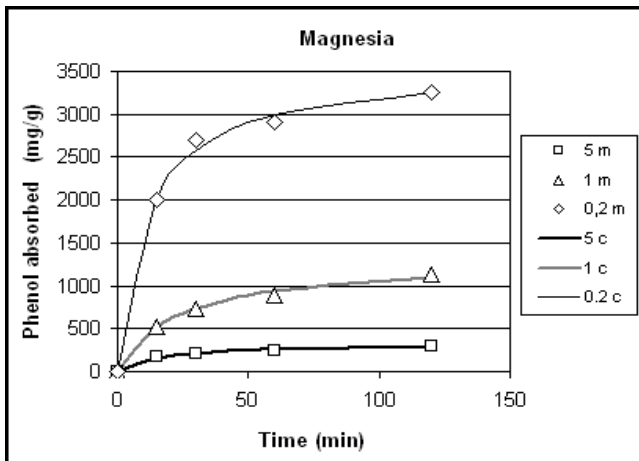


Fig. 2. Phenol absorbed per gram (g) of magnesia (m=measured value, c=calculated value).

However at small amounts of magnesia added, the phenol available is greater than that actually absorbed and this is an indication that magnesia has reached its saturation capacity which is about 3500 mg of phenol per g of magnesia. The pH variation during absorption is presented in Figure 4. Initially the pH is that of phenol and shows a gradual increase as time

passes and phenol is consumed. It finally ends to the buffering pH, about 11, of magnesia in solution.

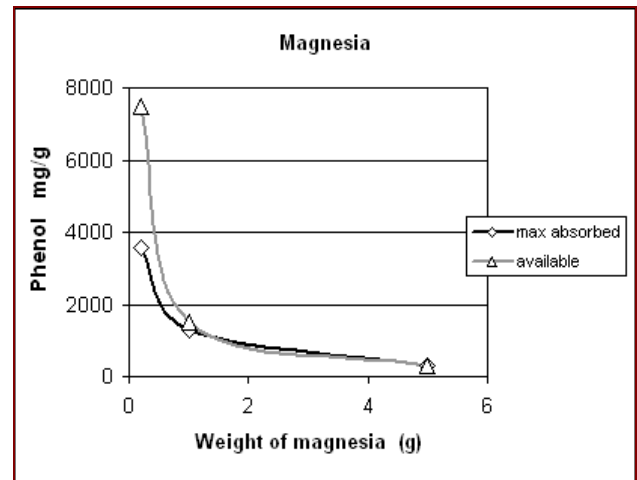


Fig. 3. Phenol available (mg/g) and maximum phenol absorbed per gram.

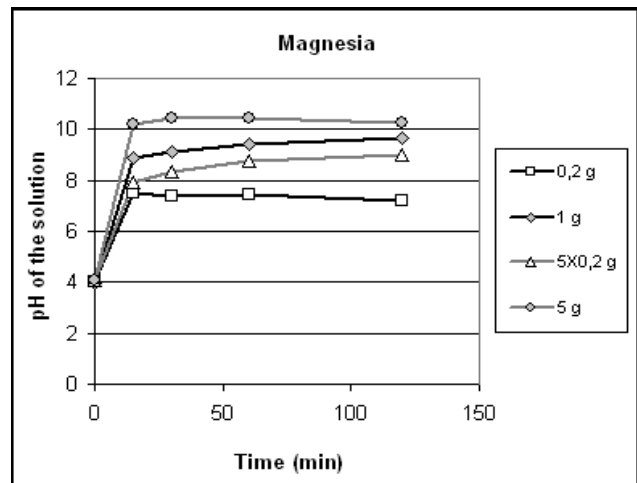


Fig. 4. pH of the solution with magnesia.

Psammitic marl

The results of phenol absorption on psammitic marl are presented in Figures 5 to 8 for three levels of absorbent addition namely 20, 10 and 5 g per litre of solution. Figure 5 presents the remaining phenol in the solution as a function of time. Although the amounts of psammitic marl used are higher than in the case of magnesia the remaining phenol is still high.

The amount of phenol absorbed per gram of psammitic marl is presented in Figure 6. The comparison of the phenol available to the maximum phenol actually absorbed is presented in Figure 7. The best absorptivity appears in the case of 5 g of absorbent per litre of solution and is about 85 mg of phenol per g of psammitic marl. Apparently the absorptivity of psammitic marl is much lower than that of magnesia. Even at psammitic marl additions as high as 20 g per litre it was not possible to absorb all the available phenol in the solution.

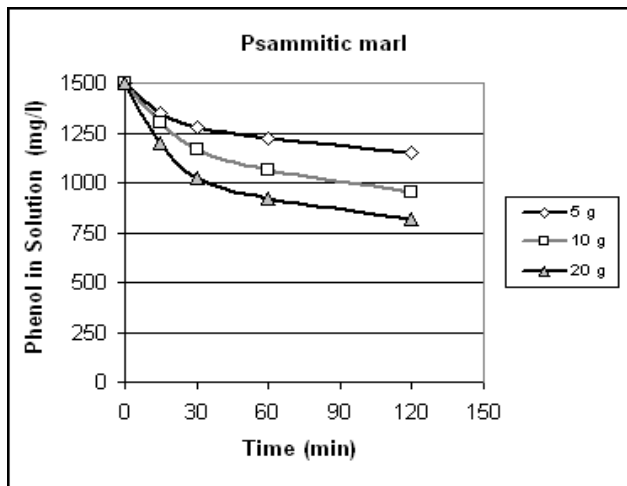


Fig. 5. Remaining phenol (mg/l) in solution.

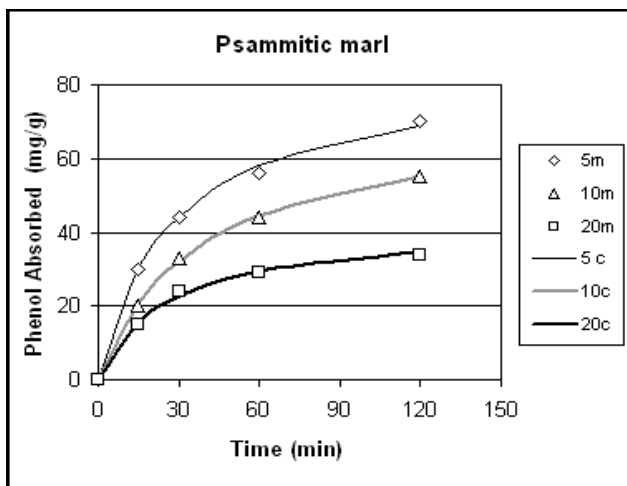


Fig. 6. Phenol absorbed per gram (g) of psammitic marl (m=measured value, c= calculated value).

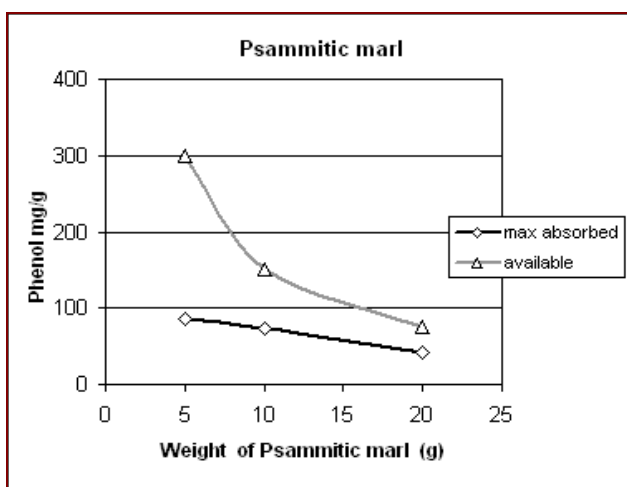


Fig. 7. Phenol available and maximum phenol absorbed per gram.

The variation of pH with time is presented in Figure 8. Here again there is a rapid increase in the beginning that slows

down and does not exceed the buffering pH, about 8, of calcite that is the absorbing constituent of psammitic marl.

Bentonite

The results of phenol absorption on bentonite are presented in Figures 9 to 12 for three levels of absorbent addition namely 20, 10 and 5 g per litre of solution. The immediate observation is that the absorbance of bentonite is much lower than the previous materials used. From Figure 11 it is seen that the maximum quantity of phenol absorbed per gram of bentonite is reached when 5 g of material is used and is of the order of only 40 mg/g. Finally the pH of the solution with the addition of bentonite comes to the buffering pH, about 8, of this material.

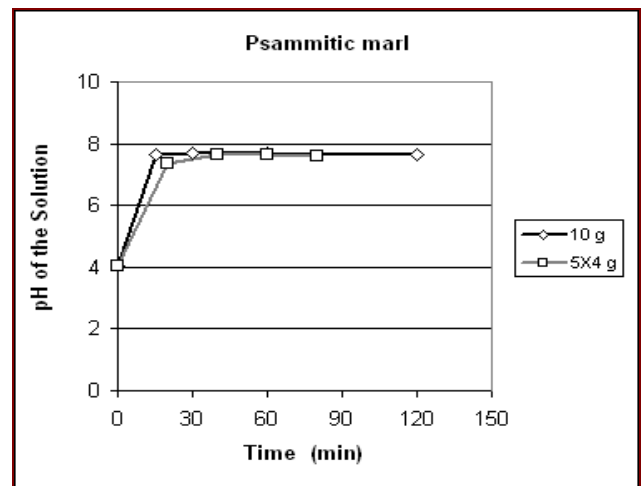


Fig. 8. pH of the solution with psammitic marl.

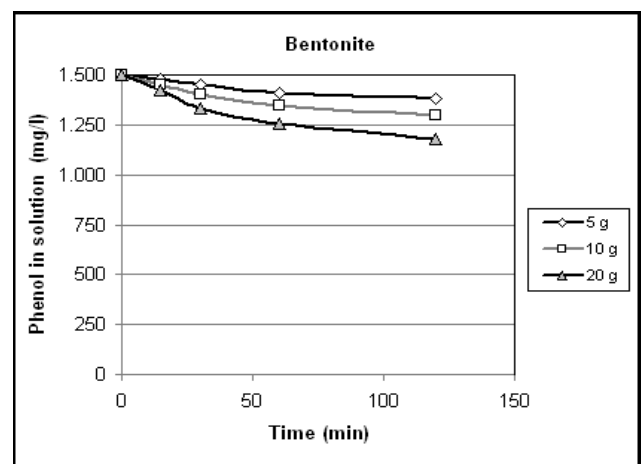


Fig. 9. Remaining phenol (mg/l) in solution.

B. Series 2: Successive absorbent additions

From the previous series of tests it is noticed that the total amount of phenol is higher when large amounts of the absorbent are used and at the same time the maximum per gram of absorbent appear at small quantities. In order to take advantage of this phenomenon, the series 2 of tests was

designed. According to this series of tests the total amount of absorbent to be used is added in stages.

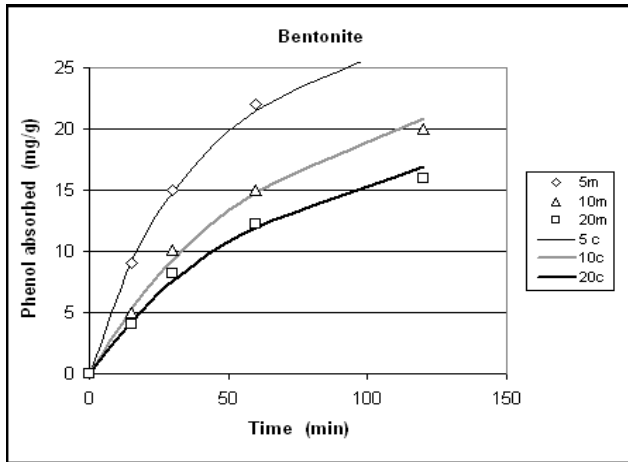


Fig. 10. Phenol absorbed per gram (g) of psammitic marl (m=measured value, c=calculated value).

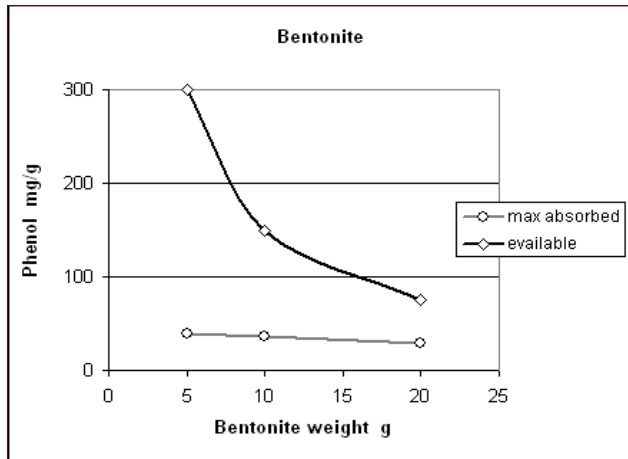


Fig. 11. Phenol available and maximum phenol absorbed per gram.

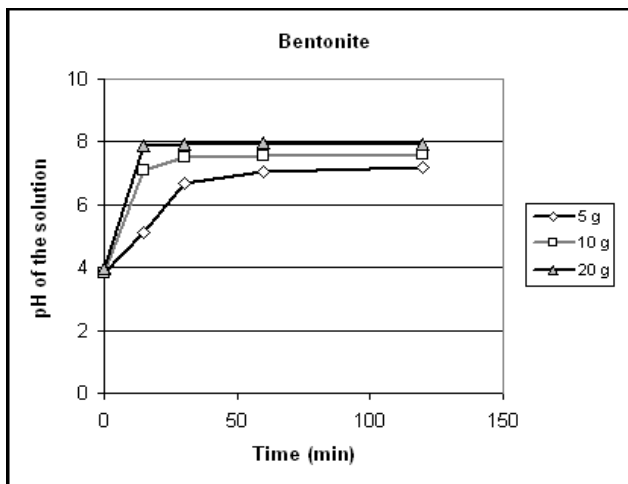


Fig. 12. pH of the solution with bentonite.

Magnesia

For magnesia we already have the absorption results for 1 g of the material. The test is repeated but the same amount of magnesia is added at 5 stages of 0.2 g at a time, every 20 minutes. The remaining phenol appears in Figure 13 and the equivalent amount of phenol absorbed per cumulative gram is presented in Figure 14. Initially there is a peak in the absorbancy that eventually peaks to the same value if sufficient time is allowed.

Psammitic marl

For psammitic marl we already have the absorption results for 20 g of the material. The test is repeated but the same amount of absorbent is added at 4 stages of 5 g at a time, every 20 minutes. The remaining phenol appears in Figure 15 and the equivalent amount of phenol absorbed per cumulative gram is presented in Figure 16. Here again there is a peak of absorbance in the beginning that eventually peaks to the same value if sufficient time is allowed.

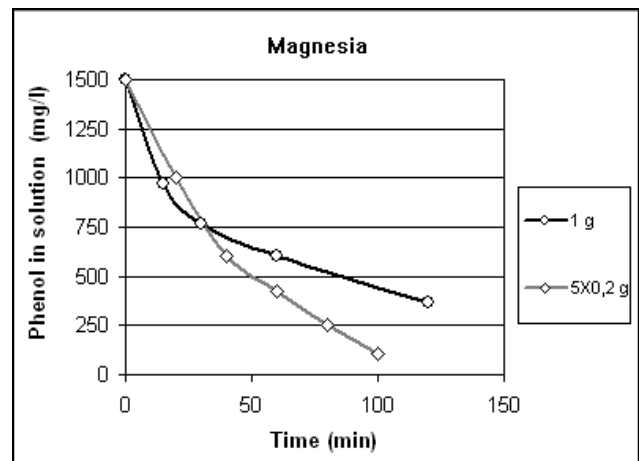


Fig. 13. Remaining phenol (mg/l) in solution.

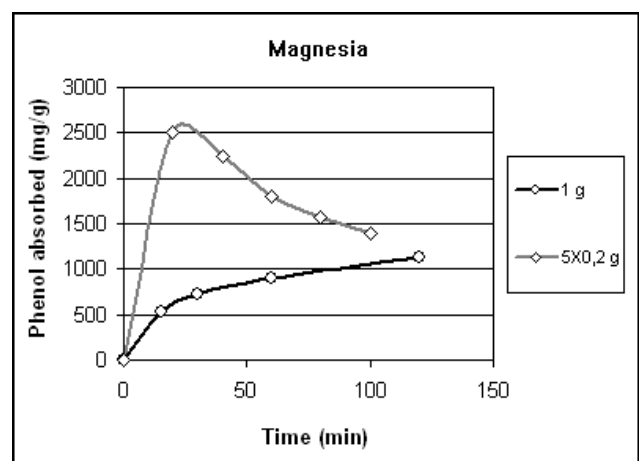


Fig. 14. Phenol absorbed per cumulative gram (g) of magnesia.

IV. MATHEMATIC MODELING

Figures 2, 6 and 10 that show the absorption curves of phenol per gram of the absorbent are typical ones of chemical

absorption. Initially they show a rapid absorption rate, indicated by the steep slope of the curves and eventually the rate slows down and the curves tend to horizontal lines that correspond to the maximum absorption that coincides with the saturation of the absorbent.

These curves can be represented by a function of time $F(t)$ that can be transformed into a straight line of the form [10],

$$F(t)/t = k \cdot [F_m - F(t)] \quad (1)$$

Where $F(t)$ is the amount of phenol absorbed per gram of the material at time t , k is a constant showing the rate of absorption and F_m is the maximum absorbance per gram of the material.

Equation (1) indicates that the cumulative absorption rate ($F(t)/t$) at time (t) is proportional to the difference between the maximum absorption and that achieved at time t .

Equation (1) can be transformed further into (2)

$$F(t)/t = k \cdot F_m - k \cdot F(t) \quad (2)$$

Substituting $Y = F(t)/t$ and $x = F(t)$ equation (2) becomes

$$Y = ax + b \quad (3)$$

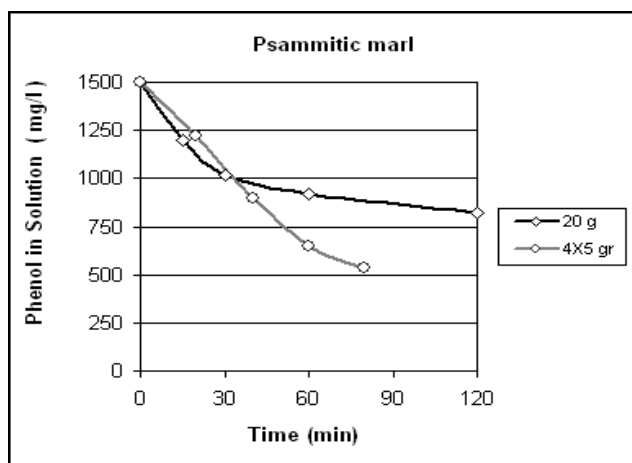


Fig. 15. Remaining phenol (mg/l) in solution.

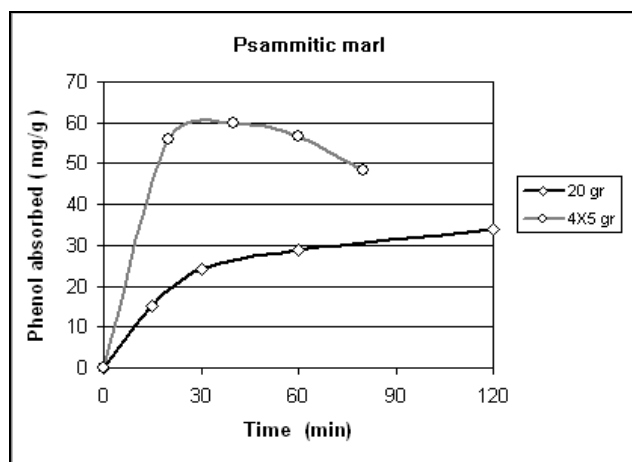


Fig. 16. Phenol absorbed per cumulative gram (g) of psammitic marl.

Plotting Y versus x one has a straight line where the slope $a=k$ and the intercept $b=k \cdot F_m$, which enables us to determine k and F_m . As an example we study the case of absorption where 5 g of each absorbent are used as shown in Figure 17.

Using the mathematical transformation, Figure 17 is transformed to Figure 18 shown below. The measured data is represented by the dots while the equivalent straight lines represent the ones calculated by the method of least squares. The slope and the intercept are shown near the corresponding line and are used to calculate the rate of absorption k and the maximum absorbance F_m of each absorbent. The calculated values are presented in Table IV.

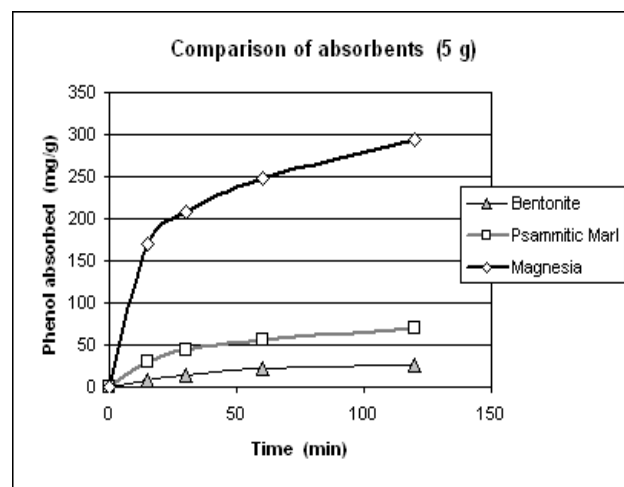


Fig. 17. Comparison of absorbents at 5 gram per litre of solution.

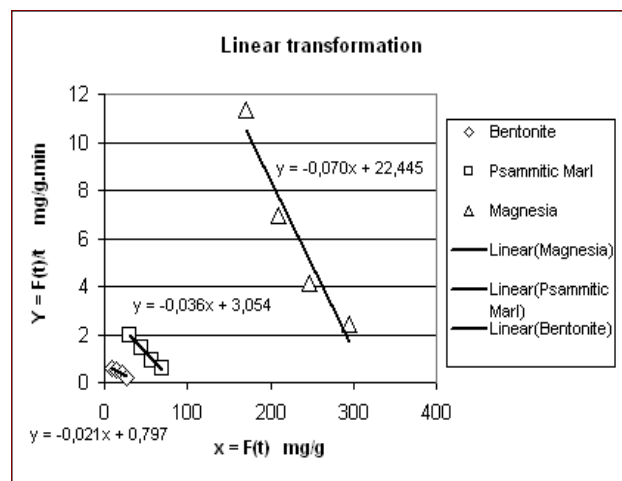


Fig. 18. Linear transformation of the absorption curves.

TABLE IV
CALCULATED CONSTANTS

Constant	Bentonite	Marl	Magnesia
k	0,021	0,036	0,070
F_m	38	85	321

By applying the values of k and F_m for each absorption case into equation (1), one can find the calculated curves and compare them with the actual measured data. This is already done in Figures 2, 6 and 10 for all the tests.

V. DISCUSSION AND CONCLUSIONS

From the results obtained it appears that the absorption of phenol on the absorbents tested is an acid base reaction on the surface of each compound used and this is indicated by the pH study.

The absorption of phenol on each absorbent has a maximum indicating that there is a saturation point probably when the surface of the absorbent is covered with a monolayer the reacting phenol that disappears from the solution.

This is a typical case of chemical absorption case and is supported by: a) the pH increase with the addition of the absorbent; b) the fact that the most basic absorbent has a better performance; and c) the existing maximum (monolayer) as already mentioned.

It is easily concluded from Table IV that magnesia has the highest absorption rate and the highest absorbance is followed by psammitic marl while the performance of bentonite is almost negligible.

In the cases studied it appears that one can increase the reaction rate by adding the absorbent in stages rather than adding the total quantity at the beginning.

Since the absorption takes place on the surface of the absorbent and does not consume the whole material one could say that the phenomenon should be described as adsorption rather than absorption.

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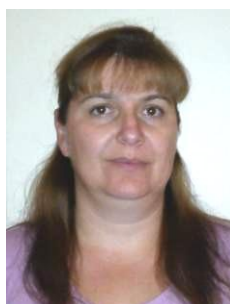
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