

PHYSICAL TREATMENT OF OLIVE OIL MILL WASTE WATERS FOR THE REMOVAL OF THE PHENOLS AND ANALYSIS OF ADSORPTION KINETICS

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ABSTRACT

Olive oil mill waste waters (OMWW) is a liquid waste produced during olive oil production. It has water soluble monomers like, tanen, polyphenols, polyalcohols and polymers. OMWW also has insoluble matter like cellulose, pectin and oil. Especially because of the hazardous effect of phenols in OMWW, phenols must be removed to prevent contamination. This study aims to look forward in the adsorption process which is a method for phenol removal.

Keywords: Adsorption, Desorption, Phenol, Olive Oil Mill Waste Waters

INTRODUCTION

Turkey is one of the biggest oil producers of the world, according to statistics 93 450 000 olive trees are present with a yearly yield of 1,5 million tons of olive fruit production capacity. But an average amount of 1-2,5 kg, depending on the system used, OMWW is produced for every 1 kg of oil production. Because of this the OMWW treatment is very important for our country and for the other producer countries.

The content and amount of OMWW depends on the maturity of the fruit, the trees, the agricultural methods for growing the trees, the quality of the soil, climate and especially to the kind of olive oil process system. In the Mediterranean area mechanical presses or three phase continuous systems are widely in operation. With the developing of the new technologies two phase continuous systems are now started to operate in the production.

Treatment methods of OMWW can be classified as physical, chemical, biological and all combination where these techniques are all used together. Main examples are aerobic, anaerobic treatments, filtration, flocculation, wet-oxidation, evaporation and adsorption. In this study the adsorption of phenols in the OMWW are analyzed and different methods are mentioned about this topic.

METHOD

Adsorption is the handling of the dissolved components in a solution on a proper interface, in other words it is a separation process in which certain components of a fluid phase are transferred to the surface of a solid adsorbent. Today different adsorbents are used with various properties like activated carbon, natural zeolite, bentonite, montmorrillonit and clay. (Stokes R.J., Evans F. D., 1997).

Adsorption processes are usually classified according to the kind of phases constituting the interface and according to the type of forces acting at this surface. Depending on the type of phases in contact, we can consider the process of adsorption in the following systems; liquid/liquid, solid/gas, liquid/gas, solid/liquid.

Adsorption has 2 basic steps, these are the transportation of the adsorbate from the bulk phase to the adsorbent and the adsorption on the adsorbent surface. First step depends on the adsorbent and solvent properties. In this step the diffusion of the adsorbate through the

adsorbent surface (external diffusion) and the adsorbents diffusion into the adsorbent capillaries (internal diffusion) must be carefully analyzed.

Adsorption from multi component solvents is a very complex process and presents many difficulties. It can be approached in two ways ; as the adsorption of a given substance from a multi component solvent or the adsorption of many substances from a given solvent. (Oscik J, Cooper I.L., 1982).

In a multi component solvent like OMWW the first approached is handled. In OMWW phenol is analyzed.

Phenols in the OMWW are resistant to bio degradation, they cause inhibition and toxicity because of this they are tried to be adsorbed on a surface (Cabrera F., 1997).

The adsorption rate depends on the size and structure , the solvent it is in, its solubility, polarity, molecular weight of the adsorbate. It is also strongly effected by the physicochemical properties of the adsorbent. For example as the molecular weight increases adsorption increases. Or a non polar adsorbate acts differently from a polar adsorbate like phenols, polar ones are harder to separate from the solution (Viraraghavan T., Alfaro M. F., 1997).

Kinetic and isotherm studies are important in adsorption. They are the main steps for discussion of the experimental datas. Kinetic studies simply shows the action of adsorption through a time interval (Jio G., Lua Chag A., 1999). Adsorption isotherm is the equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent particles at a given temperature (McCabe W.L.,1985).

Most common isotherm models are Langmuir and Freundlich isotherm models.

Langmuir linear isotherm model equation; $1/q_e = 1/Q^0 + 1/b Q^0 1/C_e$

q_e ; amount adsorbed at equilibrium (mg/gr)

C_e ; equilibrium concentration of the adsorbate (mg/l)

Q^0 (mg/gr) and b (lt/mg) are the Langmuir isotherm constants related to the maximum adsorption capacity and the energy of adsorption, respectively.

Freundlich linear isotherm model equation; $\ln q_e = \ln k_F + 1/n \ln C_e$

Where k_F (mg/gr) $(lt/mg)^{1/n}$ and $1/n$ are Freundlich constants related to adsorption capacity and adsorption intensity, relatively of the sorbent.

ADSORPTION STUDY WITH DIFFERENT ADSORBENTS

Activated carbon has a wide usage in the treatment processes and it can be made from different raw materials like olive seed, olive stone, peat, palm. Pulp, husk and some other materials. It is produced in high temperatures about 800-850 °C and carbonation made as the last step (Lafi K.W.,2000).

In a laboratory study the adsorption is examined on the activated carbons produced from olive seed and olive pulp. Phenol, COD and pH parameters are analyzed during the experiments. Some activated carbons are made by single step thermal activation, some modified by urea and some treated by nitrogen/steam mixture. Experiments are done in 50 cm³ beakers with addition of 20% dilute OMWW and different amounts of activated carbons at 25°C and data is taken for 48 hours. Kinetics and isotherm studies are made. Also the sample activated carbons are classified according to their surface structure and iodine number and their adsorption ability are analyzed. When the datas are studied it is seen that carbons with well developed porosity especially in the mesopore region favor phenol adsorption, while the carbons with well- developed microporosity favor total organics adsorption, for the complex system of OMWW. For carbons with similar mesoporous structure the adsorption of phenols might be effected by their chemical nature, namely by the higher number of carbonyls. The latter might be effect adsorption of total organics by activated carbons with microporous structure. Data obtained from kinetic studies were fitted to Lagergren equation and the distribution coefficients have been also estimated. Isotherm data fit well to the Langmuir model with the

exception of carbon treated with urea that follows a multilayer adsorption obeying Freundlich isotherm (.Gliatsatao P.,2002).

It is well known that activated carbon has a distribution of sites with varying activation energies. According to Polanyi's potential theory, the adsorbate is loaded first on the high energy sites and subsequently on lower energy sites, the contaminants sorbed on the lower activation energy desorb were quickly than those at higher energy sites and desorption rate can be approximated (alberty a., 1987).

Addition to the adsorption-desorption is also examined in the studies. In a study by bentonite the data showed that desorption increases with decreasing aqueous concentration. The hysteresis between adsorption and desorption indicates the presence of irreversible adsorption. These results indicate that desorption was greatly dependent on substituted groups of aromatic compounds. On the other hand compounds with an electron attracting group showed no hysteresis and the desorption was reversible. Phenol which has hydroxyl groups belongs to the electron donating group.

The potential of bentonite to adsorb phenol from aqueous solution was assessed and seen that the adsorption capacity dependent strongly on the PH of the solution, as pH decreased the adsorption capacity increased.

The limiting case of this favorable isotherm is irreversible adsorption, where the amount adsorbed is independent of concentration down to very low values.

All systems show a decrease in the amount adsorbed with an increase in temperature and of course adsorbate can be removed by raising the temperature even for the cases labelled irreversible. However desorption requires a much higher temperature when the adsorption is strongly favourable or irreversible than when the isotherms are linear (McCabe W.L., 1985). In another laboratory study focused on the main chemical and physical characteristics of OMWW and the treatment by adsorption. Adsorption are applied on samples pretreated by sedimentation configuration and filtration. Activated clay is to be used as the adsorbent, the effect of treatment will be stated as percent reduction of phenolic content and percent reduction of organic load. The supernatant was filtered using Whatman-4 filter paper on vacuum setup under 500 mmHg. The clay samples were enriched to 70% montmorillonite (smectite) using hydro-cyclones. They placed in a solution either containing hexa-decyl-trimethyl-ammonium-bromide or tetra-methyl- ammonium-chloride while immersed in water both for 24 hr. Then dried at 70°C and milled to 150 µm later calcined at 450°C for 2 hr and screened 85 µm (Al-Mallah K.,2000).

The experimental apparatus is made of 16 tightly glass tubes bundled on a rocking assembly and 50 ml samples are treated with activated clay at 35°C and the pH, COD and phenol content are recorded. It is seen that the more organic the solute the higher the tendency to adsorb on filter media so ionic and polar solutes are left in solution leading an increase in the conductivity. The reduction COD and BOD values are due to the adsorption of high molecular weight organic molecules on to the solids in the sludge or onto filtering media. Also as the concentration of activated clay increased the phenol reduction increased resulting an increase in pH value. The more hydrophobic a substance is the more likely it is adsorb, and a hydrophilic substance is less likely to adsorb. Centrifugation and filtration showed effectived reduction of total solid content and reduce some phenolic and organic contents and peaks are showed during the adsorption process maximum, the effective removal achieved at 4 hr and a removal of 81% phenol and 71% organic matter is reached (Al-Mallah K.,2000).

In another study for the physical treatment of OMWW the effect of various adsorbents, filtration and centrifugation on phenol content was studied. Following adsorbents were used for the removal of phenolic compounds from OMWW.

Activated Carbon

ACI : methylene <300 , Iodine value: 850-900, granular (1 mm²)

ACII : methylene <300, Iodine value: 850-900, powder, 40 µm diameter pore size.

ACIII : methylene >300, Iodine value:1000, 40 µm diameter pore size.

1. Tonsil tonsil and zeolites are not modified
2. Zeolite

Different amounts of adsorbant were treated with OMWW by using the following steps. After the treatment process total phenol and o-diphenol content were analyzed.

Adsorbant	Control	1%	2%	3%	5%	4%
(gr)	-	0,5	1	1,5	2	2,5
OMWW (ml)	50	50	50	50	50	50

Samples are taken to 25°C , 200 rpm, 24 h mixing, centrifugation (9000 rpm, 15 min), precipitate and filtrate is separated and the filtrate is analyzed for total phenol and o-diphenol.

The effect of adsorbant ratio on total phenol content and o- diphenols are given in Fig.1 and Fig 2. Total phenol content decreased with the increasing adsorbant concentrations. Activated carbon II and III (ACII and ACIII) with a concentration of 5% seemed to be the most effective adsorbants for the removal of total phenolic and o-diphenolic compounds. AC II and AC III caused 60 and 57 % decrease in total phenol content and 66, 61.7 % in o-diphenol content, respectively. The phenol removal efficiencies of tonsil and zeolite were quite lower than ACII and ACIII. ACI which is in a granular form didn't effective as compared to ACII and ACIII because of its lower surface area. Although 60 % total phenol removal was obtained, there was no decolorization observed in OMWW samples.

Figure 2 Effect of Adsorbant Ratio on o-diphenol Content

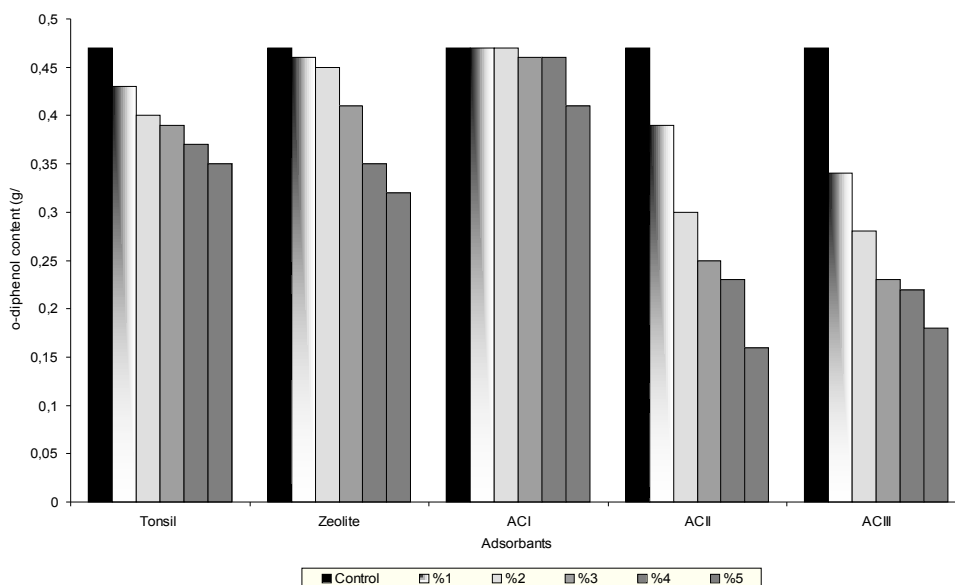


Figure 1: total phenol analysis

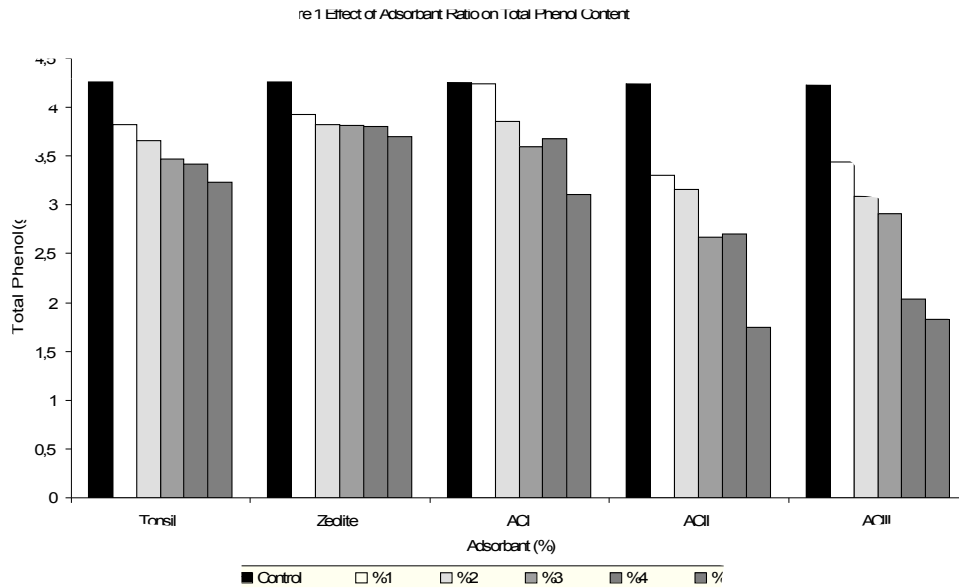


Figure 2: o-difenol analysis

Samples were filtrated through cellulose acetate filter and total phenol content was analyzed in the filtrate. The properties of the filters are given below;

F1 : 20 μ m pore size, Cellulose Acetate filter

F2 : 40 μ m pore size, Cellulose Acetate filter

Samples are filtrated with 20 and 40 μ m pore size cellulose acetate filter and total phenol analysis made.

After the filtration process 14,5 % phenol removal was achieved when F1 type of filters were used whereas the fenol removal ratio was only 3,53 % when F2 type filters were used.

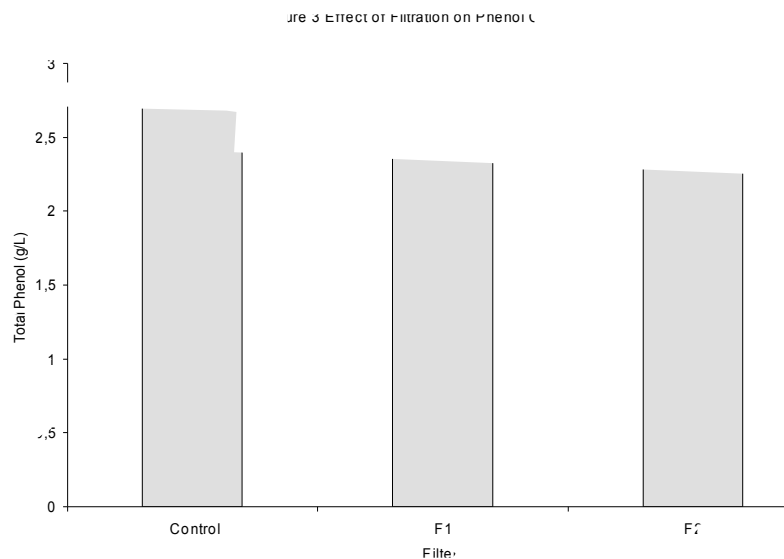


Figure 3: filtration effect on total phenol content

The effect of centrifugation time on phenol content was studied. In the first set of experimentes OMWW samples were centrifugated at 9000 rpm. for 5 minutes repeatedly.

Figure 4 shows the change in total phenol content in each 5 min. intervals. Although the centrifugation time was extended to 25 min. (5 times for 5 minutes) there was no considerable decrease in total phenol content. The phenol removal was 10,5 % 25 minutes.

In the second set of experiments OMMW samples were centrifugated at 9000 rpm for 10, 15, 20, 25 minutes respectively. As shown in Figure 4. the decrease in phenol content was only 5,1 % for 25 minutes.

As a result , the repeated or direct centrifugation at various time intervals did not effect total phenol content to a large extend.

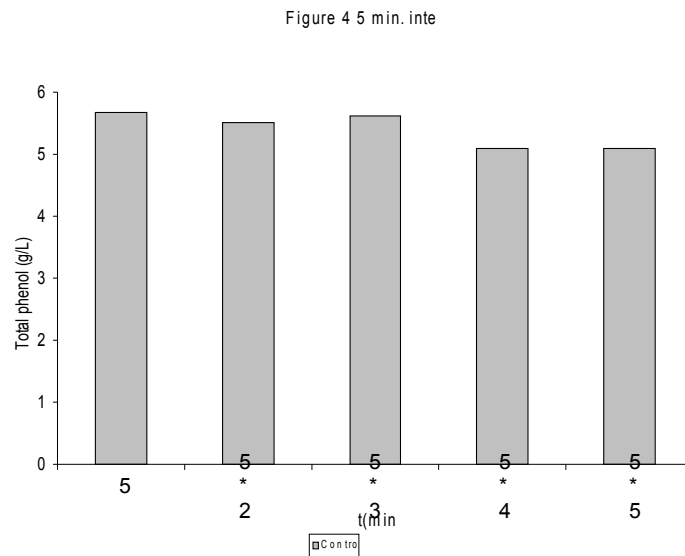


Figure 4: effect of centrifugation on total phenol content

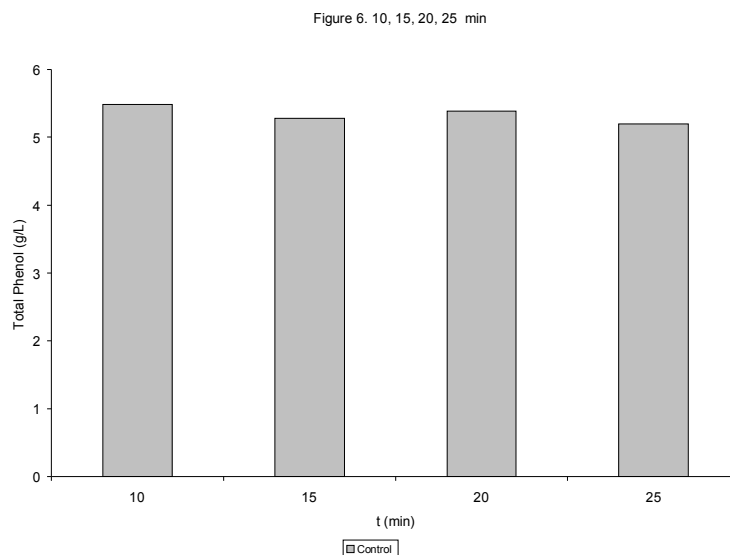


Figure 5: effect of continuous centrifugation on total phenol content

RESULT

According to the studies the treatment of OMMW with various adsorbents are analysed. It is obvious that the usage of adsorbents have a strong reduction with the economic load of the

process. Today it is becoming a new area to work with cheaper and easily produced adsorbents like natural zeolites, activated carbons from wastes and the feasible regeneration of these adsorbents because of this adsorption studies will become more important through the coming years as a member of recycling and hazard prevention.

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