

USE OF MODIFIED BENTONITE FOR PHENOLIC ADSORPTION IN TREATMENT OF OLIVE OIL MILL WASTEWATER*

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Abstract– Natural and modified clays were applied as adsorbents for the removal of organic contaminants from wastewater. This study presents an investigation on the technical feasibility of using modified minerals that are named organoclay for treatment of dissolved substances, mainly polyphenols in olive mill wastewater. The different parameters such as applied cation dosage were effective on the removal of contaminants by these adsorbents (%CEC), pollutant concentration, pH and particle size of minerals. In this investigation bentonite particles were modified by stirring the clay with a long chain quaternary ammonium cation. Doses of the applied cation varied from zero to 1.5 times the clay CEC. Results from tests using 40 g/L of natural minerals with CEC=90 milliequivalent/100g, ground clay with less than 0.2 mm size in solution, and pH=3, showed that the removal of polyphenols from olive mill wastewater and orthodiphenol from synthetic wastewater were 22% and 30% respectively. By using 40 g/L organo-bentonite modified with benzyl dimethyl hexadecyl ammonium bromide (BDHDA) and an applied cation dosage equal to 50% CEC for the removal of total polyphenols and orthodiphenol from industrial and synthetic wastewater, with particles less than 0.2 mm, after the mixture was shaken for about 24 h at room temperature and pH=3 using a rotary shaker resulted in 80% and 88% maximum reduction of contaminants from industrial and synthetic wastewater respectively.

Keywords– Polyphenols, organoclay, adsorbent, olive mill wastewater

1. INTRODUCTION

Widespread contamination of wastewater by hydrocarbons and organic chemicals has become a recognized problem of global importance in recent years. These compounds are nonpolar and hydrophobic in nature, their aqueous solubility limits are significantly greater than the maximum contaminants level value. For this reason, removal of these organic pollutants from wastewater has been the subject of many studies [1].

A combination of clay minerals and polymeric flocculants has been successfully used for suspended solids removal from wastewater [2]; however, removal of dissolved solids using such technologies is inefficient. Therefore, there remains an incentive to develop internal treatment technologies to remove dissolved contaminants in closed cycle wastewater systems to affect further contaminant reductions [2].

One type of montmorillonitic clay, bentonite, is characterized mainly by an Al octahedral sheet placed between two Si tetrahedral sheets. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the clay. This charge imbalance is offset by exchangeable cations, typically Na^+ and Ca^{2+} at the clay surface. The layered structure of the clay facilitates expansion after wetting. Na^+ and Ca^{2+} ions in the presence of water, result in a hydrophilic environment at the clay surface. Consequently, natural bentonite is an ineffective sorbent for nonionic organic compounds (NOC) in water, with a high surface area [3].

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The hydrophobicity of natural minerals can be increased by replacing the cations Na^+ and Ca^{2+} , normally present with organophilic quaternary ammonium cations which arrange tailored clay [4]. Tailored clays in this fashion have shown high capability in organic contaminant removal such as aromatic hydrocarbons, chlorinated alcohols and chlorinated hydrocarbons from contaminated soils and hazardous waste [5,6]. Application of tailored minerals in adsorption offers several advantages including: large mineral deposits, relatively low cost of minerals and cations, possible regeneration, long-term stability and versatility in the preparation of tailored minerals for target pollutants [7].

In this study, the use of a modified bentonite (organo-bentonite) for phenolic removal from olive oil mill wastewater was investigated. The performance of this adsorbent in the treatment of natural and synthetic wastewater was compared.

2. MATERIALS AND METHODS

a) Bentonite and amine

The inorganic compound that was utilized in this research was a kind of bentonite which was bought from the Novin-Chimiar Co. Benzyl dimethyl hexadecyl ammonium bromide (BDHDA), with 98% purity manufactured by Aldrich Chemical Co. with a $\text{N}(\text{C}_7\text{H}_7)(\text{CH}_3)_2(\text{C}_{16}\text{H}_{33})^+\text{Br}^-$ formula were used. All experimental analysis were effected in parallel and the averages of the data were reported.

b) Determination of cation exchange capacity

2 g of dried bentonite was weighed and placed in centrifuge tubes. 15 ml 0.1M CaCl_2 solution was added into the tubes. The tubes were shaken in a thermostat shaker for 24 h at 25°C , and then centrifuged at 6000 rpm for 30 min. The liquid was discarded and the clay was subsequently saturated with Ca^{2+} three times. Clay was washed with distilled water repeatedly until it became free from Cl^- and then Ca^{2+} was extracted with a 15 ml solution of 0.1 M BaCl_2 three times. The concentration of Ca^{2+} was determined by an atomic absorption spectrophotometer (Model: Varian 220) at 422.7 nm. Results showed that CEC value was 90 meq/100 g clay.

c) Preparation of organo-bentonite

For the preparation of organo-bentonite, 50 g of pretreated bentonite was mixed with BDHDA in a 2 L stainless steel reactor equipped with baffles and a mechanical stirrer at 65°C for 30 min. The amount of consumed amine versus CEC% of mineral clay is reported in Table 1. Cation dosages varied in range from 0 to 150% CEC. The treated bentonites were separated from water by centrifugation at 6000 rpm within 20 min and then washed three times with distilled water. The samples were dried at 100°C and mechanically ground to pass through a 100-mesh screen. The appropriate equation for brevity of Table 1 is: $Y = 2.525 X$, where X is CEC% and Y is gBDHDA/100 g clay.

Table 1. Amounts of amine used for preparation of organo-bentonite

CEC%	0	25	50	75	100	125	150
g BDHDA/100 g clay	0	9.9	19.8	29.7	39.6	49.5	59.4

d) Preparation of wastewater

Two different wastewaters have been used in this research, a synthetic and an olive mill wastewater from an olive oil factory. For a synthetic medium, orthodiphenol in various concentrations were studied. The wastewater from the olive mill unit contained contaminants such as nitrogen, phosphorous, phenolic substances, fat and soluble organic compounds. The quality of the produced wastewater from the olive

mill was strongly influenced by the oil production process, centrifugation or pressing [8]. The industrial wastewater was supplied from the Roudbar olive oil factory located 15th km of the Rasht-Roudbar road. The oil was processed in this factory with the pressing method and the approximate analysis of its wastewater is shown in Table 2. For adjustment of the pH of both samples, HCl and NaOH were used.

Table 2. Specifications of Roudbar olive oil wastewater [8]

Parameter	Value (mg/L)
Total COD	40000-200000
BOD	65000-70000
Polyphenols	1200-3000
Orthodiphenol	300-400
Nitrogen	100-1000
Dissolved Phosphorus	150-400
Fat	1000-15000
Alkalinity	200-500
pH	4-6

Filtration was utilized as a procedure to reduce the solid particles. Filtering a type of wastewater with a remarkable amount of suspended particle proved to be a useful method for reducing the amount of pollutants. The filtration of olive mill wastewater by Wattman paper No. 4 caused COD, total polyphenol and orthodiphenol decrease by 11.5, 9.8 and 3.5% respectively.

e) Extraction of phenolic compounds from olive mill wastewater and analysis

To extract the phenolic compounds from the olive mill wastewater, 100 ml of the sample was acidified up to pH=2 with HCl and then extraction with 20 ml ethylacetate at 25°C three times was done. The sample was dried by contact with 2 g sodium sulphate crystals for 30 to 40 min. The ethylacetate left in the extract was vaporized in a rotary evaporator and the residual solution was mixed with 50 ml of a mixture of water/methanol 40/60 volumetric ratio, respectively [9]. The final solution was a liquid which contained all the phenolic compounds of the olive mill wastewater.

Over 20 types of phenolic compounds (polyphenols) have been identified in the olive oil. Concentration of these compounds is measured by spectroscopy using a UV-visible absorption device. The proportional quantity of different kinds of phenolic compounds in the wastewater sample is unpredictable, so a comprehensive standard solution could not be provided. For measuring total polyphenol, the sample extracted by ethylacetate was measured by a spectrophotometer at 725 nm and by using a standard curve for 3,4 dihydroxy benzoic acid, total polyphenol could be determined [10]. On the other hand, among all types of phenolic compounds only orthodiphenol has a very different maximum absorptive wavelength, so its concentration was measured separately than that of the rest together [10].

To measure the amount of orthodiphenol, first 2 ml of 5% sodium molybdate solution, dissolved in 50% ethanol was added to 10 ml of the sample wastewater. After 15 min at 20°C the absorption was measured at 370 nm by a UV-visible spectrophotometer (model: S-2130, KOREA) which is the maximum absorptive wavelength of orthodiphenol, with respect to the blank solution [10].

The 3,4-dihydroxybenzoic acid, a phenolic compound in olive oil, was chosen as the base compound and the standard diagram for it at 725 nm was provided. At this step, 5 ml of sodium carbonate solution

(200 g/L) and 2.5 ml Folin-Ciocalteu phenol reagent were added to 50 ml of the sample. After 60 min the absorption was measured at 725 nm which is the maximum wavelength of 3,4-dihydroxybenzoic acid at 20°C in glass vials. By using water instead of the sample and doing the foregoing steps, the blank solution was prepared. The standard diagram was plotted by preparing different-concentrated solutions of 3,4-dihydroxybenzoic acid in a mixture of water-methanol 40/60 volume ratio [10].

The absorption curve versus concentration of orthodiphenol was plotted and fitted with the following equation in which X and Y stand for concentration (ppm) and absorption respectively.

$$Y=0.59412X+0.46534$$

The effect of organoclays on the removal of phenolic compounds from industrial wastewater was studied. 25 ml of wastewater was passed through 1 g of absorbent which was prepared with amine. The amounts of total sorbed pollutants from wastewater was measured using the standard curves.

f) Orthodiphenol concentration measurement in the synthetic wastewater by gas chromatography (GC)

GC is quite sensitive and introducing the olive mill wastewater with its high concentration was impossible, so in this investigation, a synthetic wastewater was prepared by making several samples, with various concentrations of orthodiphenol with regards to its concentration in the olive mill wastewater. Sorption of orthodiphenol on the natural and modified bentonite was conducted using a batch equilibration technique. 2 g of natural bentonite and 10 ml of various synthetic wastewaters or 1 g of modified bentonite and 10 ml of wastewaters were added to 20 ml glass centrifuge tubes. Then the tubes were capped air tight. To obtain equilibrium, solutions were placed on a shaker for 24 h at 20°C. After equilibration, the aqueous phase was separated by centrifugation at 6000 rpm for 20 min. A volume of 5 ml supernatant was extracted with 15 ml of methanol, then orthodiphenol was analyzed by GC with specifications given in Table 3. The removal efficiency of the pollutant and sorbed pollutant were determined in these experiments.

Table 3. Specifications of gas chromatograph

Injection temperature	Oven temperature	Detector temperature	Detector	Column	Model
200°C	200°C	250°C	FID	SBP-5	Chrom pack cp 9001

Removal efficiency of the pollutant is the ratio of the removed pollutant with BDHDA treated bentonite to the original amount of pollutants. The sorbed amount of the pollutant is the amount of removed pollutant per gram of treated and untreated clay. All the graphs are plotted by the error bars in this investigation.

3. RESULTS AND DISCUSSION

In a preliminary investigation, natural bentonite was modified with BDHDA cation applied in doses varying from 0 to 150% of the mineral CEC. Figure 1 presents the effect of cation exchange capacity (%CEC) on the removal efficiency of poly and orthodiphenol. Increasing cation dosage causes the increase of removal efficiency from 22 to 80% and 30 to 88% for polyphenols and orthodiphenol respectively. 50% CEC shows the maximum pollutant removal. Pollutant adsorption increased rapidly in the range from 0 to 50% CEC, above which the cation dosage had no effect on their adsorption.

Figure 2 presents the sorption isotherms of orthodiphenol from water onto the unmodified bentonite and BDHDA-bentonite at 50% saturation of the mineral CEC. The adsorption of orthodiphenol on the

BDHDA-bentonite corresponds to the L-type isotherm in Giles' classification [11], reflecting a relatively high affinity between the adsorbate and adsorbent. The relatively high affinity between orthodiphenol and BDHDA-bentonite is probably the result of the orthodiphenol molecules interacting favorably with the benzene ring in the BDHDA ion through increased π - π type interaction [12]. Isotherm of unmodified bentonite is linear while the isotherm of BDHDA-bentonite is nonlinear and shows that orthodiphenol sorption increases with increased substitution of BDHDA ion for inorganic cation in the interlamellar space of the clay. Compared to the unmodified bentonite, the intercalated BDHDA ions can accumulate more tightly on the interlamellar surfaces on the bentonite to form a nonpolar organic carbon surface for higher orthodiphenol sorption. For this reason the saturated sorption of orthodiphenol by BDHDA-bentonite was 54 mg/g which is higher than that by unmodified bentonite, 22.5 mg/g respectively.

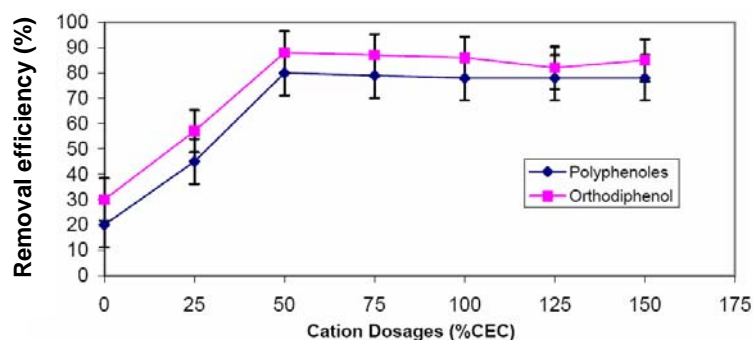


Fig. 1. Removal efficiency of polyphenols and orthodiphenol with BDHDA bentonite vs. cation dosages with standard error bars. Conditions: pH=3, particle size=0.2 mm, initial poly phenols conc.=1500mg/L, initial orthophenol conc.=350 mg/L and clay conc.=40 g/L

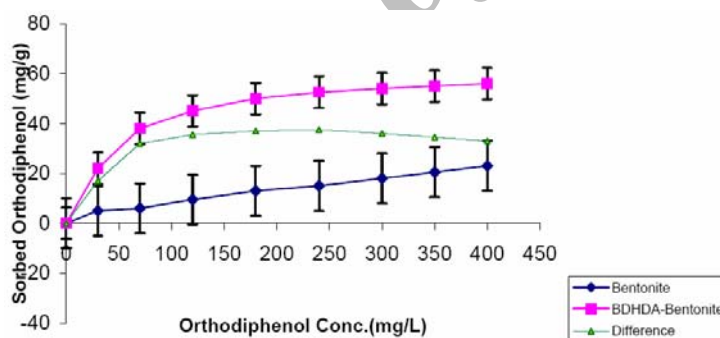


Fig. 2. Sorbed isotherms of orthodiphenol on BDHDA Bentonite and unmodified Bentonite with standard error bars. Conditions: pH=3, particle size=0.2 mm, and BDHDA dosage=50% CEC

Figure 3 presents the percentage of polyphenols removal by BDHDA-bentonite at different equilibrium values of pH. The maximum adsorption of phenolic compounds occurs at $\text{pH} \leq 3$, and by increasing pH, adsorption decreased regularly. Above $\text{pH}=7$ the adsorbed amount was negligible. Noting that various pollutants are present in olive mill wastewater, the reason for this observation is completely apparent, but probably the presence of functional groups related to some compounds in wastewater such as COOH and OH and their conversion to carboxylate and phenolate form ($-\text{COO}^-$ and $\text{C}_6\text{H}_5\text{O}^-$) at pH above 3 could be the reason for the intensive decrease of adsorption. Also carboxylate and phenolate ions are organophobic and generally don't show any affinity for adsorption.

The effect of aggregate sizes of modified bentonite on orthodiphenol removal efficiency is presented in Table 4. Aggregates smaller than 0.2 mm were the most efficient, with a maximum removal of 88%. Crocker *et al.* [13] showed that aggregates smaller than 0.5 mm increased the desorption rate of naphthalene bound to HDTMA-tailored smectite. Furthermore, it seemed that, in the present study, the removal efficiency of 0.5-1 mm aggregates was not statistically different from that of 1-1.5 mm and 1.5-2

mm aggregates. As smaller particles have more surface areas than bigger particles, there is an increase in the efficiency of the reaction between amine and mineral clay, and consequently, the removal efficiency of polyphenols is increased.

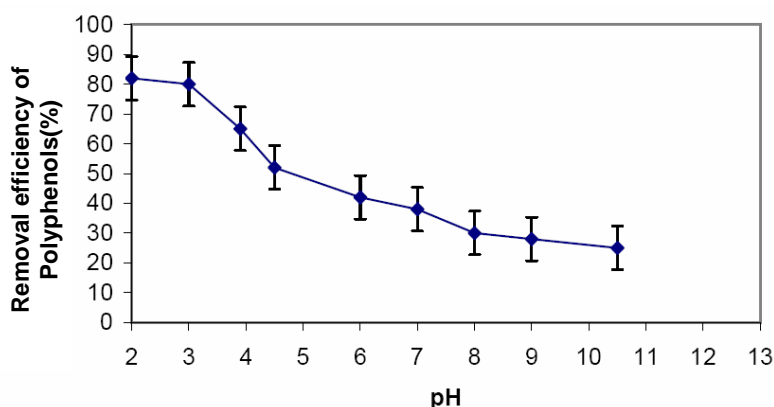


Fig. 3. Removal efficiency of polyphenols vs. pH of solution with error bars. Conditions: initial polyphenols conc.=1500 mg/L, particle size=0.2mm, Clay conc.=40 g/L and BDHDA dosage=50% CEC

Table 4. Effect of aggregate size of BDHDA-bentonite on orthodiphenol removal from synthetic wastewater

Aggregate size (mm)	Orthodiphenol removal efficiency (%)				
	Applied cation dosage (expressed as mineral CEC)				
	0%	50%	75%	100%	150%
≤0.2	30	88	86	84	81
0.5-1	13	67	73	63	70
1-1.5	14	62	64	59	66
1.5-2	6	55	52	56	58

4. CONCLUSION

The experimental results of this study indicate the feasibility of removing polyphenols from olive mill wastewater using BDHDA modified bentonite. The different parameters such as applied cation dosage, pollutant concentration, pH and particle size of minerals were effective on the efficiency of the removal of contaminants. Maximum polyphenol removal was observed with a cation dosage equal to 50% CEC. It was observed that the adsorption of phenolic compound was highly affected at $\text{pH} \leq 3$. 88% of orthodiphenol removal from synthetic wastewater. Maximum removal efficiency was obtained with particle size equal or less than 0.2 mm.

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