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New tailor-made bio-organoclays for the remediation of olive mill waste water

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Abstract. A systematic study aimed at obtaining new organoclays for the treatment of Olive Mill Waste water (OMW) has been performed. Several organoclays have been prepared by loading different amounts of the biocompatible surfactant Tween20 onto the K10 montmorillonite (MMT). Complementary kinetic and equilibrium studies on the adsorption of the Tween20 onto the MMT have been carried out and the characterization of the new tailor-made bio-materials has been performed by means of the XRD and FT-IR measurements. Finally the prepared bio-organoclays have been successfully applied for the OMW remediation and they proved to be highly effective in decreasing the organic content (OC) to an extent that depends on both the amount of loaded surfactant and the experimental protocols applied.

1. Introduction

Treatment of Olive mill wastewater (OMW), generated by the olive oil extraction process, is becoming a serious environmental problem [1]. Thus, there is a continuous request to find proper protocols to be applied for the treatment of OMW in order to achieve efficacious and less expensive remediation methods. Clays, organoclays and nano-composites had been proven effective in the removal of organic pollutant [2].

Bearing in mind these considerations, the present study has been undertaken in order to apply a new class of tailor-made surfactant-clays complexes prepared for the decontamination of OMW. As surfactant we have chosen the bio-compatible nonionic polyoxyethylene surfactant Tween 20 while the versatile K10 montmorillonite (MMT) has been employed as clay support.

The Tween/MMT complexes have been synthesized, characterized from a physico-chemical point of view and useful applied to the OMW treatment.

2. Experimental

All the reactants were obtained from Sigma-Aldrich and utilized without further purifications. The OMW was kindly provided by Oleificio Gianbanco (Carini, Palermo, Italy). Samples were collected in closed glass containers and, after two weeks sedimentation, centrifuged at a speed of 5000 rpm for 20



min using a IEC CL31 Multispeed centrifuge. The obtained supernatants were filtered and stored in dark bottles, at 4°C, for further treatment.

The organo-clays were prepared by mixing in different ratios the aqueous surfactant solutions with the aqueous clay suspensions at room temperature. The mixture was stirred for 24h and the resulting organo-clays were separated from the mixture by centrifugation, dried open air for 48h and finally crushed with hammer and ground in a ceramic mill.

Equilibrium and kinetic studies were performed by means of the spectrophotometric method with a diode-array Analytic Jena S600 spectrophotometer equipped with thermostated compartments for 1.00 cm cuvettes and an appropriate magnetic stirring apparatus.

The experiments were performed at 25 °C in the pH range 1.0-5.0.

XRD measurement were performed with a Philips PW 1729 system (Ni filtered Cu K α radiation, $\lambda=1.5406 \text{ \AA}$, scan rate = 0.01°/sec).

Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) spectra of air-dried samples of Tween 20 adsorbed on MMT were measured in a Nicolet Avatar 320 FTIR, using a MIRacle ATR device with a diamond crystal plate (Pike Technologies, Madison, WI).

The OMW's treatment was performed by adding a weighted amount of either the MMT or organo-modified clays to a proper volume of OMW under constant stirring for 7 hours at T=25 °C. Two different protocols have been implemented: in the first the OMW sample has been treated with 15 mg/ml of Tween/MMT clay for two hours (single step) while in the second the OMW samples has been treated twice with 7.5 mg/ml of bio-organoclay for two hours (two-steps treatment). In order to establish the reduction of organic load, the resulting mixtures have been filtered through 0.22 μm cellulose membrane filters and the UV-vis spectra of the solutions has been recorded.

3. Results and discussion

3.1. Kinetic and equilibrium studies. The adsorption kinetics of the Tween20 onto the MMT have been investigated by means of the spectrophotometric method under constant stirred conditions by changing the surfactant concentration in the range $(1.0 - 5.0) \cdot 10^{-3} \text{ mol dm}^{-3}$ while the amount of clay was kept constant at 0.36 mg mL^{-1} . In Fig. 1 a typical kinetic profile is reported.

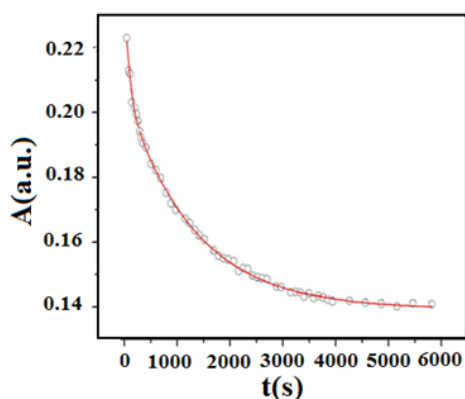


Fig.1. Typical adsorption kinetics of Tween 20 onto MMT. T=25.0 °C, pH = 4.0.

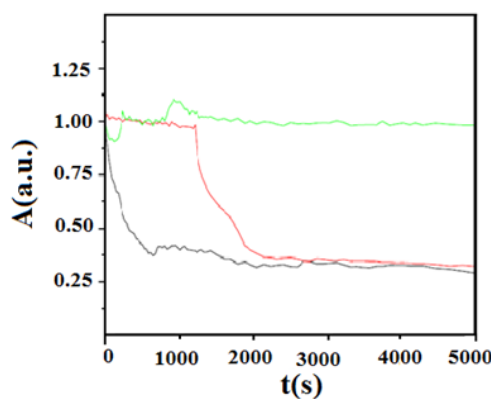


Fig.2. Coalescence kinetics of organo clays prepared with 0.045 (black line), 1.0 (red line) and 5.0 (green line) mmol/dm $^{-3}$ of Tween 20 onto MMT. T= 25.0 °C, pH = 4.0.

The quantitative analysis of the kinetic data, performed by applying a protocol based on advanced statistical diagnostics [3], revealed that according to the literature [4-5], the adsorption kinetics follow a pseudo-second order model and yield the values of the kinetic constants as $k = 1.8 \cdot 10^{-3} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is almost independent of the surfactant concentrations as well as on the pH values.

Perusal of Fig 2 clearly shows that the obtained bio-surfactant/clays revealed to be much more stable to coagulation than the unmodified MMT.

Since all systems reached the equilibrium state, the absorbance values have been used to construct the adsorption isotherms. It has been found that the adsorption occurs accordingly to a Langmuir isotherm. The obtained values of the sorption parameters, which have been found to be independent of the pH values, are $K_L = 200 \pm 40 \text{ dm}^3 \text{ mol}^{-1}$ and $q_m = (2.0 \pm 0.2) \cdot 10^{-4} \text{ mol g}^{-1}$

Moreover, the analysis of the equilibrium data by means of the Dubinin–Radushkevich (DR) equation yields a value of the mean free energy of adsorption (E) as $E = 12 \pm 1 \text{ KJ mol}^{-1}$, which, according to the literature [6-7] allow us to draw the conclusion that chemisorption of the biosurfactant onto MMT occurs.

3.2. XRD Characterization. In Fig.3 the XRD patterns of the MMT clay both in the absence and in the presence of the Tween 20 surfactant are depicted.

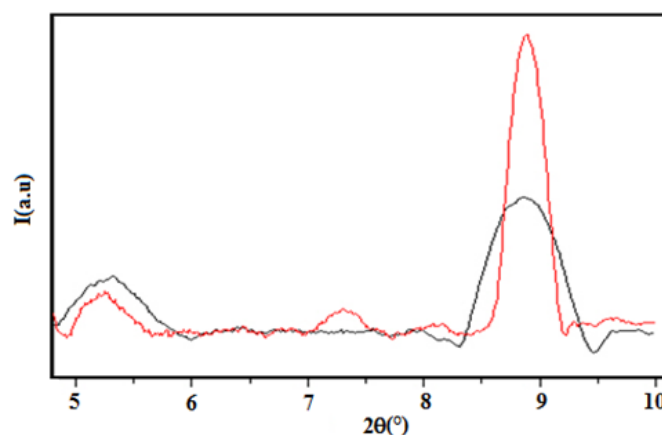


Fig.3. XRD patterns for parent MMT (black line) and MMT functionalized with Tween 20 (red line) at $T=25.0 \text{ °C}$ and $\text{pH}=4.0$.

Modification of the MMT with the nonionic surfactant leads to the appearance of an additional reflection peak at $2\theta = 7.33^\circ$ ($d=12.04 \text{ \AA}$) which is indicative of the successful intercalation of this compound, which displace the intercalated water molecules from the interlayer spaces [8-9].

3.3. FTIR Characterization. Fig 4 shows peak resolution of pure surfactant (left) and surfactant added to MMT (right). It can be seen that the adsorbed surfactant exhibits a relative decrease in the symmetric methyl stretch. Our hypothesis is that the methyl group vibrations might be hindered due at the internal part of the adsorbed micelle structure.

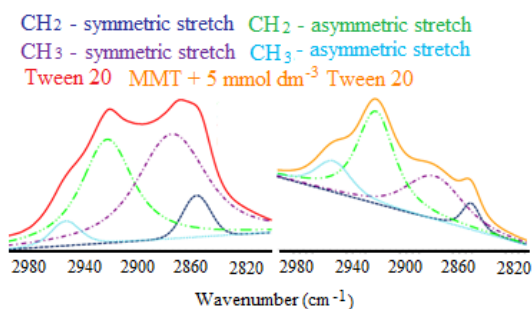


Fig.4. FTIR spectrum of the aliphatic stretching including resolution of pure surfactant (left) and surfactant added to MMT. Assignment based on Ref.10.

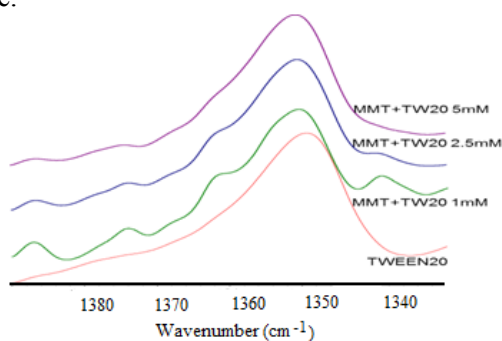


Fig.5. FTIR spectrum of the $-\text{CH}_2$ deformation vibrations of pure surfactant and surfactant/MMT complexes.

Additional perturbations on the $-\text{CH}_2$ vibrations of the adsorbed surfactant can be seen in Fig 5, where it can be observed that the peak at 1381 cm^{-1} , usually assigned to hydrated methyl groups [11] is not observed at none of the samples. The peak at approximately 1350 cm^{-1} is related to methylene wagging vibrations of the gauche conformation and appears in all samples, while those at 1362 and 1340 cm^{-1} (and presumably also the peak at about 1388 cm^{-1}) provides information about the trans of the alkane chain. The relative peak intensity of those bands decreases with increase amount of surfactant. This could indicate that the trans conformation of the alkane chain decreases when there is a large amount of Tween20 on MMT.

3.4. OMW treatment. The surfactant modified clays have been successfully employed for the treatment of the OMWs samples. It has been observed that the prepared bio-organoclays are slightly more effective in decreasing the organic content (OC) with respect to the unmodified MMT and that the organic content decrement is directly dependent on the amount of clay used (Fig. 6) Moreover, the results shown in Fig. 7, reveal that the two steps-treatment leads to a larger reduction in the organic content. Since in both cases quantities of organoclay were equal, it appears that the double-step treatment might be more efficacious than the single step application, as long as time is not a limiting factor.

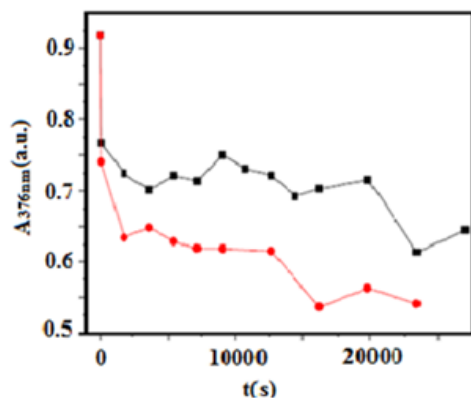


Fig.6. Typical OC's adsorption kinetics into 5 mg/ml (■) and 15 mg/ml (●) MMT. T=25.0 °C, pH = 4.0.

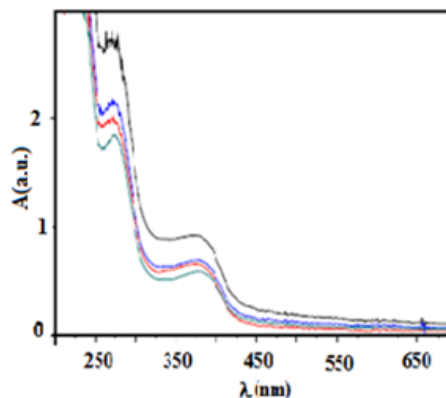


Fig.7. UV-vis spectra of untreated OMW (black line), oMW treated by means of protocol 1 (red line) and protocol 2 (blue and green line for the first and the second step respectively). T=25.0 °C, pH=4.0.

4. Conclusions

The present work is part of a wider research project aimed at finding the more promising system able to remove undesired organic compounds from waste waters.

The results obtained revealed promising and effective for proposing appropriate protocols by using new tailor-made organoclay for the decontamination of the OMW.

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