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Research Article

Adsorption and removal of Acid orange 7 using industrial essential oil solid by-products of melissa (*Melissa officinalis*) and yarrow (*Achillea millefolium*)

Ivanka Hambarliyska^{1✉}, Dimitrios Manousakis², Gergana Marovska¹, Adelina Bylianova¹, Anton Slavov¹

¹Department of Organic and Inorganic Chemistry, Technological Faculty, University of Food Technologies, 26 Maritsa Blvd., Plovdiv, 4002 Bulgaria

²Department of Chemical Engineering, University of Western Macedonia, Koila, 50150, Kozani, Greece

Abstract

Melissa (M) and yarrow (Y) essential oil industry residual biomass was used for decontamination of Acid Orange 7 (AO 7) in model system. Both residues were rich in dietary fibers (DF): the amount of total DF determined for M and Y were $75.26 \pm 0.98\%$ and $80.39 \pm 1.37\%$, respectively and the soluble DF were $4.59 \pm 0.57\%$ and $5.04 \pm 0.43\%$, respectively. The adsorption process reached equilibrium at the 10th min (1 g M or Y, 20 mL dye water solution ($1 \text{ mg} \cdot \text{mL}^{-1}$, pH 3.63). The adsorbed amount of AO 7 for M was $19.39 \pm 0.12 \text{ mg} \cdot \text{mL}^{-1}$ (96.95% efficiency) and for Y: $19.04 \pm 0.24 \text{ mg} \cdot \text{mL}^{-1}$ (95.20% efficiency). The lower pH favored the decontamination: for M at pH 1.21, the efficiency was 98.70%, and for Y at pH 3.63: 98.55%. Pretreatment of the M and Y residues with 0.1 N HCl led to increase of the adsorption capacity. Both residues compared with three well known adsorbents - aluminum oxide, chromatographic silica gel and activated carbon, showed almost the same efficiency of removal as activated carbon. These results suggested that the M and Y by-products could be successfully employed as renewable and readily available adsorbents for decontamination of water systems containing AO 7.

Keywords

acid orange 7, melissa (*Melissa officinalis*), yarrow (*Achillea millefolium*), biosorption, decontamination

Abbreviations

AO 7 – Acid orange 7; M – melissa residue; Y – yarrow residue; PUC – polyuronide content; DE – degree of esterification.

✉Corresponding author: Ivanka Hambarliyska, Department of Organic and Inorganic Chemistry, Technological Faculty, University of Food Technologies, 26 Maritsa Blvd., Plovdiv, 4002 Bulgaria, tel.: +359 899650256; E-mail: vanya.hambarliyska@gmail.com

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Introduction

Water is one of the most valuable resources on the planet and its purification and use for drinking and domestic purposes, in agriculture and industry is emerging as one of the great future problems worldwide. Various industries, such as chemical, pharmaceutical, textile, metal mining, agricultural, food processing, etc., use large quantities and generate waste water, which is often highly polluted and, without being purified, cannot be discharged into nature, as it represents a serious risk (Elgarahy et al. 2023). In particular, the textile manufacture is among the most water-demanding and the wastewater is highly contaminated with the dyes (mostly synthetic) that are used to dye the fabrics. Azo dyes are the most widely used organic class of pigments that find application in various industries, including textile and food industries (Rathi and Kumar 2022). They are characterized by the presence of one or more azo groups in the structure of the compounds. Azo dyes are synthesized from aromatic amines by diazotization, and a large part of the starting substances are toxic and carcinogenic, and also over time, azo dyes in nature can break down to some of the starting precursors (Crettaz et al. 2020).

Some of the azo dyes have a toxic effects on humans, as well as on terrestrial and aquatic organisms. Therefore, there is a great need to treat wastewater containing azo dyes in order to eliminate them or convert them into safer products (Benkhaya et al. 2020). Some of the coloring substances employed showed mutagenicity and carcinogenicity. Visible light, temperature and microorganisms degrade them slowly or do not have pronounced effect on their structures, turning these compounds in a dangerous contaminants. Consequently, it is important to develop effective methods to remove these substances from wastewater.

Acid orange 7 (AO 7) belongs to the azo type compounds. It has bright, attractive orange-red color. Industrially it is applied for dyeing silky and wool-type and paper-based products, polyamides, for toner formulations, leathers, hairstyling formulas, and in biology for chemical staining (Crettaz et al. 2020). *p*-Aminobenzenesulfonic acid (precursor for the preparation of AO 7) was found in thirty seven cloths ranging from 100 to

442 mg.kg⁻¹ (Crettaz et al. 2020). Brüscheiler and Merlot (2017) give insights on the possible mutagenicity of aminobenzenesulfonic acids (both *o*- and *p*- isomers). Traces were found in different colored fiber matters.

Methods used for wastewater treatment include coagulation, flocculation, sedimentation, membrane filtration, electrochemical techniques, and more. (Taheri et al. 2022). One of the most used worldwide is conventional microbiological treatment (activated sludge) followed by ozonation. However, most of these techniques are not 100% efficient, nor are they financially profitable, being quite resource-intensive (Kumar and Ahmad 2011).

Adsorption, as a treatment process for pollutants decontamination, has high efficacy and low-cost characteristics. It is not volumable and is not affected by toxic chemicals. Adsorption processes also allow in some cases regeneration, recovery and reuse of adsorbents (Nascimento et al. 2014). In addition, frequently waste biomass of the agricultural industry (e.g. essential oil production) can be used as nature-friendly, bio-degradable, inexpensive and disposable adsorbents. Adsorption of azo dyes occurs by different mechanisms, thanks to the ways of interaction of the adsorbent and the contaminant due to van der Waals forces, formation of hydrogen bonds, hydrophobic or electrostatic interactions, etc. Two main ways of carrying out the process can be distinguished - adsorption under static conditions (when the adsorbent is placed in a suitable container and the contaminated solution is added; stirring is often used to intensify the adsorption) (Ouakouak et al. 2021) and under dynamic conditions (when the adsorbent is placed in a suitable vessel (most often a column) and the contaminated solution is passed through it by gravity or with the help of a pump) (Khan et al. 2022). Adsorption under static conditions is an easier method to perform, but the disadvantage is the batch mode of operation. Adsorption under dynamic conditions is performed in a continuous mode, periodically changing the adsorbent after reaching its capacity to retain the target pollutant.

Various techniques and approaches were applied for AO 7 decontamination. Among them bio-degradation using the enzymatic machinery of microorganism, oxidation, light-induced degradation and adsorption with numerous

adsorbents were the most often used (Perera 2019). The bio-degradation has several advantages: economical, useful and simplicity to a certain extent, but also is often accompanied with some drawbacks (slow degradation, finding suitable microorganism's settings, relatively spacy areas). Besides, some microorganisms degrade AO 7 to toxic products, which further needed to be purified (Gottlieb et al. 2003). Oxidation (chemically or photo-induced) has advantages related to fast degradation of AO 7 and related compounds. In the same time it has some limiting shortcomings related to expenses of treatment, highly reactive oxidizing agents and generation of highly reactive radical species. The process also lead to production of toxic compounds, such as naphthoquinones, phthalates, etc. (Perera 2019; Xu et al. 2011). The most often investigated approach for AO 7 decontamination is adsorption. Various materials were examined as adsorbents and the best results were obtained with activated carbon and nanocomposite materials (Khalil et al. 2024; Nistor et al. 2022; Perera 2019). However, these materials are expensive and preferably wastes and by-products from power plants, agricultural and food industry could be an alternative (Gupta et al. 2006; Kaya and Şahin 2022; Marovska et al. 2023; Naraghi et al. 2017; Pelosi et al. 2013). A great number of biomass from agriculture have been used for decontamination in model or real systems of water contaminated with azo dyes – sunflower seeds, potato leaves, durian seeds, orange, banana, potato, pumpkin, cucumber and melon peels, hazelnut shells, coffee waste, residues from sugar beet processing, citrus peels, wheat straw, bamboo wood, activated carbon from by-products obtained during the processing of plant raw materials, etc. (Amalina et al. 2022). Research has been done on the application of distilled rose flower (Rabbani et al. 2016) and lavender waste biomass (Slavov et al. 2023) for the treatment of wastewater from the textile industry. In all cases considered, the free energy of the process is negative, which indicates the spontaneous nature of the adsorption (Marovska et al. 2023).

In the scientific literature, some data on the application of post-distillation melissa and yarrow by-products for the purification of waters contaminated with azo dyes, such as AO 7, exists, but they are scarce. This gave us grounds to test the

hypothesis of the possibility of using these residues as an effective adsorbent for azo dyes.

Materials and Methods

Materials. The melissa (*Melissa officinalis*) and yarrow (*Achillea millefolium*) solid residues were obtained from essential oil distilling company Galen-N (Zelenikovo, Brezovo district, Bulgaria, 2022). After end of distillation residues were taken away from the distillation vessel, dried, and stored at $20 \pm 2^\circ\text{C}$.

AO 7 (Sodium 4-[(2-hydroxynaphthalene-1-yl)-diazanyl] benzenesulfonate) was obtained from local distributors.

Preparative methods. The dried melissa - M and yarrow - Y were milled with a laboratory milling machine. The residues were pretreated with deionized water, acetone and 0.1 M HCl according to Marovska and Slavov (2023). The adsorbents used, had particle size in the 50-100 μm range.

1) Contact time impact on AO 7 adsorption. The AO 7 decontamination procedure was performed according to Marovska and Slavov (2023). After filtration of the samples the adsorption at wavelength of 500 nm was assessed (LLG-uniSPEC 2 UV-Vis spectrophotometer, LLG Labware, Germany). The concentration of the unabsorbed AO 7 was determined with the help of a calibration curve, plotted with dye's aqueous solutions with specified concentrations.

2) pH medium impact on AO 7 decontamination. Solutions of AO 7 at $1 \text{ mg}\cdot\text{L}^{-1}$ in the following solvents were used: 1. pH 1.21 - 0.1 M H_2SO_4 ; 2. pH 3.63 - aqueous dye solution; 3. pH 5.49 – 50 mM citrate buffer; 4. pH 8.30 - 50 mM phosphate buffer; 5. pH 12.80 - 0.1 N NaOH. The experiments were carried out as described previously for the influence of the contact time with the adsorbent. The parameters used were: contact time 40 min, initial azo dye concentration: $1 \text{ mg}\cdot\text{mL}^{-1}$ (total volume twenty mL), adsorbent amount: 1 g; 20°C and agitation speed 100 rpm. After the end of the incubation, filtration and measurements were carried out as described in 1). For each of the used solutions of AO 7 with a different pH, a standard curve was prepared in the corresponding solvent (and the solutions also served to reset the spectrophotometer), according to which the

concentrations of the unabsorbed azo dye were calculated.

3) Temperature impact on the AO 7 decontamination. Temperature effect on AO 7 decontamination was investigated at six different values: 0, 20, 40, 60, 80 and 100°C. The contact time was 40 min; initial azo dye: 1 mg.mL⁻¹ (total volume used 20 mL); adsorbent: 1 g; pH: 3.63; agitation speed 100 rpm. After incubation, filtration and measurements were performed analogously as described in as described in 1).

4) Pretreatment/type of adsorbent impact on the AO 7 decontamination. The influence of the type of adsorbent/pretreatment of the raw material on the AO 7 adsorption was carried out using the following adsorbents: activated carbon (Himtex Ltd., Dimitrovgrad, Bulgaria), Al₂O₃ and silica gel (Reanal, Budapest, Hungary), by-products from lavender (after steam distillation), washed with deionized water (L); rose by-products (after steam-water distillation) washed with deionized water (RD); both L and RD residues were kindly provided by Galen-N (Zelenikovo distillery, region of Plovdiv, Bulgaria, 2022 harvest). The parameters were: contact time 40 min; initial concentration: 1 mg.mL⁻¹ (20 mL volume); amount of adsorbent: 1 g; 20°C; pH: 3.63; agitation speed 100 rpm. After incubation, filtration and measurements were performed analogously as described in 1).

Analytical methods. The protein amount in M and Y residues was assessed by the Kjeldahl method using UDK152 (Velp Scientifica, Italia) and factor for multiplication of nitrogen 6.25. The PUC and DE of the by-products were determined as described in Marovska et al. (2024). The dietary fibers quantities (total, soluble, and insoluble, respectively abbreviated as TDF, SDF and IDF) were assessed with K-TDFR-100A enzymatic kit (Megazyme, Ireland) and the instructions provided by the manufacturer.

Statistical analysis. The data were averaged after three replications and presented as mean value ± standard deviation. For statistical analysis was used one-way ANOVA test (Tukey's post hoc test; $p < 0.05$) using Microsoft Excel 2013 with installed XL Toolbox NG.

Results and Discussion

Preliminary characteristics of the raw materials.

The solid residues from the essential oil industry resulted from steam and steam-water distillation or extraction with solvents (organic or liquefied gases) usually consists primarily of lignocellulosic matrix and small portions of protein and pectic type polysaccharides (Vasileva et al. 2018). The dietary fibers amounts in most of the cases is above 50-60 % with predominant quantity of IDF. The amount of SDF is in the 1-5% range. The preliminary characteristics of the melissa and yarrow by-products, resulted from the essential oil industry suggested that they are not exception from the above-mentioned observed data (Table 1). The amount of TDF determined for M and Y residues were 75.26±0.98 % and 80.39±1.37%, respectively and the SDF were 4.59±0.57% and 5.04±0.43%, respectively. The protein content for both residues were similar: 6.69±0.24% for M and 6.33±0.38% for Y by-products. The PUC, usually associated with the pectic polysaccharides in the cell walls, for both by-products was similar – around 15%, and the DE was above 85%.

Contact time impact on AO 7 adsorption. Three types of M and Y residues were used as adsorbents: the first one washed with deionized water, second - washed with 0.1 N HCl and the third one - washed with acetone. These pretreatments were performed to remove low-molecular substances from the M and Y raw materials. The choice of the solvents was based on the assumption to use liquids with different pH and also to have water-based and organic solutions for the initial pretreatments of the by-products.

Kinetic of the adsorption process of AO 7 by M and Y residues was studied first. The time in which the residues interact with the pollutant is an important parameter. The results from the experiments were presented in Fig. 1 for M and Fig. 2 for Y by-products.

The adsorption as a process is based on interactions based on physical and chemical character of the adsorbent matrix and the adsorbed substance functional groups. These interactions emerged firstly on the free sites present on the surface of the adsorbent. In the beginning of the process the unoccupied sites are much higher and usually the process is taking place very fast when the free

energy is negative (parameter showing the spontaneous character of the process) (Marovska et al. 2023).

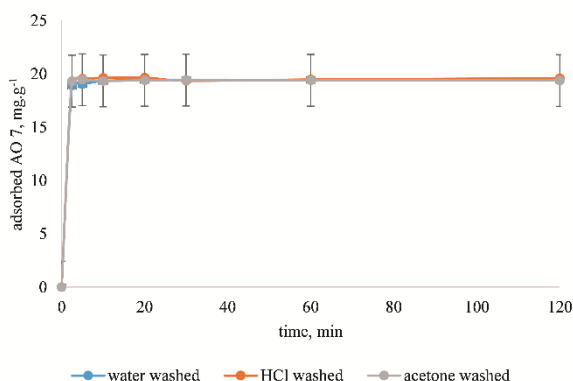


Figure 1. Contact time impact on AO 7 adsorption by melissa residues washed with deionized water, 0.1 N HCl and acetone

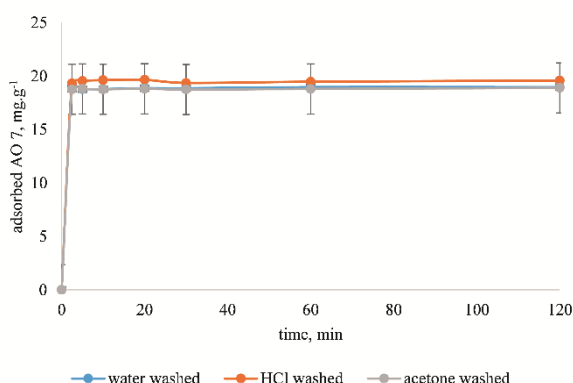


Figure 2. Contact time impact on AO 7 adsorption by yarrow residues washed with deionized water, 0.1 N HCl and acetone

When the free adsorbent sites are occupied with the adsorbed substances the process enters state of equilibrium and the concentration is known as equilibrium concentration. In our case the equilibrium time for both M and Y residues was established between 5th and 10th min (slight increase of the adsorption was observed until the 60th min but

it was negligible). The observed equilibrium concentration for M adsorbent was 19.39 ± 0.12 mg.mL⁻¹ (96.95% efficiency) and for Y adsorbent: 19.04 ± 0.24 mg.mL⁻¹ (95.20% efficiency). No significant differences between the adsorption behavior of the three pretreated M adsorbents was observed while for Y the raw material pretreated with 0.1 N HCl showed slightly higher capacity of adsorption. These results suggested that the M and Y by-products could be successfully employed as cheap, renewable and readily available materials for decontamination of AO 7 aqueous mediums.

pH medium impact on AO 7 decontamination.

Furthermore, the pH medium impact on AO 7 decontamination was investigated. Decontamination was performed at five pH values: from highly acidic conditions - 1.21 to highly basic pH - 12.80 (Fig. 3 - M adsorbent; Fig. 4 - Y adsorbent). The results suggested that the pH below 5 favors the adsorption process for both adsorbents. The highest adsorbed amount of AO 7 was observed at pH 1.21. In both cases, the adsorbents washed with 0.1 N HCl and water showed better efficiency than acetone-washed materials.

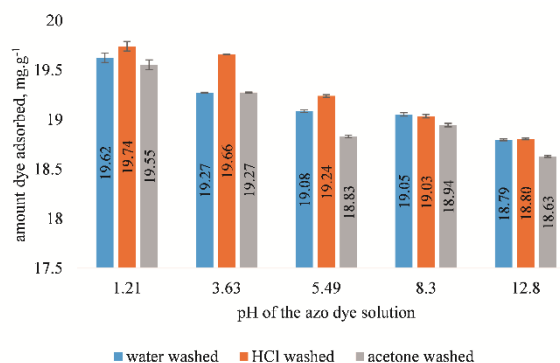


Figure 3. pH medium impact on AO 7 decontamination by melissa residue

Table 1. Characteristics of melissa and yarrow by-products

By-product	PUC, %	DE, %	TDF, %	IDF, %	SDF, %	Protein, %	Ash, %
M	14.98 ± 0.86^a	85.60 ± 3.56^a	75.26 ± 0.98^b	68.50 ± 0.88^b	4.59 ± 0.57^a	6.69 ± 0.24^a	8.66 ± 0.38^a
Y	15.48 ± 1.04^a	87.20 ± 2.47^a	80.39 ± 1.37^a	74.87 ± 1.19^a	5.04 ± 0.43^a	6.33 ± 0.38^a	5.96 ± 0.06^b

M: Melissa (*Melissa officinalis*); Y: Yarrow (*Achillea millefolium*); PUC: polyuronide content; DE: degree of esterification; a,b - Different letters in a column suggest statistically different values;

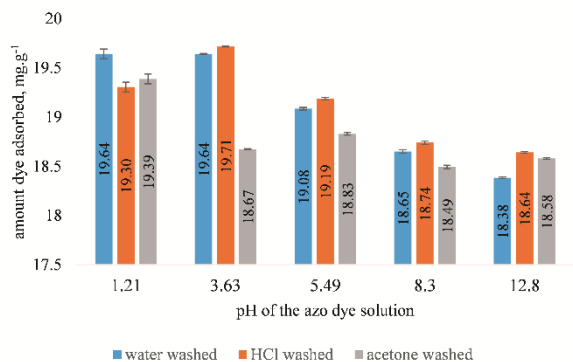


Figure 4. pH medium impact on AO 7 decontamination by yarrow residue

These results were in accordance with the data obtained by Marovska et al. (2023), Wu et al. (2011) and Pelosi et al. (2013) researching decontamination of AO 7 by rose and lavender by-products generated by essential oil industry, spent yeasts from brewery manufacturing and residues from the plant water butterfly wings, respectively. Still, yet the effectiveness of the adsorption even at higher pH was 94% for M residue and 93.2% for Y residue. These results could be explained with the decrease of the electrostatic repulsion between the AO 7 (having an ionic character and at lower values of pH the negative charge of the sulfo groups is going to decline) and the adsorbents. If we consider that pectic polysaccharides and proteins are bearing the main charges, at lower pH values the carboxyl groups will be protonated and the amino groups will have a positive charge, thus the repulsion forces will be lowered and the adsorption process - favored. In opposite - at higher pH values the dye will be negatively charged, the carboxylic groups from pectins and proteins too, and the repulsion forces will dominate. We should not forget however, that between the dye and the lingo-cellulosic matrix in the adsorbents the interactions are not electrostatic and this explains the observed adsorption even at higher pH.

Temperature impact on the AO 7 decontamination. The temperature in general had a slightly negative effect on the adsorbed amount of AO 7 and this trend was more visible observed for Y adsorbent (Fig. 5 and 6). For the M residue the highest capacity was shown by the by-product washed with 0.1 N HCl and the effectiveness of the adsorption was retained in all of the temperature interval 0-100°C. For the Y residue better

adsorption performance showed the residue washed with deionized water in the temperature interval of the measurements but the decrease of effectiveness was more pronounced. Similarly, Marovska et al. (2023) observed that the impact of the temperature on the adsorption of AO 7 on distilled rose and lavender by-products followed the same negative trend with temperature increase. These observations tentatively could be due to reversibility of the process and desorption process starts to dominate over adsorption with temperature increase.

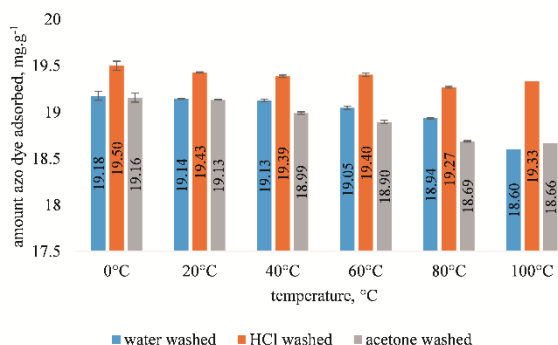


Figure 5. Temperature impact on the AO 7 decontamination by melissa residue

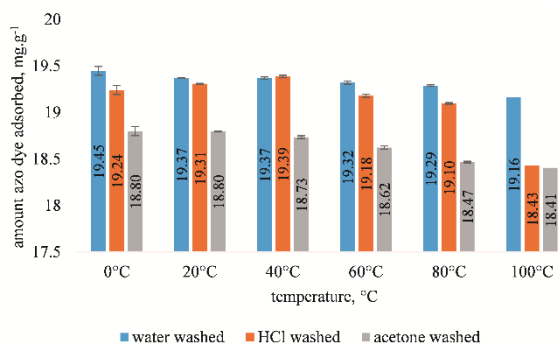


Figure 6. Temperature impact on the AO 7 decontamination by yarrow residue

Pretreatment/type of adsorbent impact on the AO 7 decontamination. In the next experiments a comparison of the effectiveness of the by-products of M and Y (and the three pretreated by different solvents their residues) and other adsorbents (three well known substances - aluminum oxide, chromatographic silica gel and activated carbon; and residues from industrial distillation of *Rosa damascena* (RD) and *Lavandula angustifolia* (L)) was performed (Fig. 7).

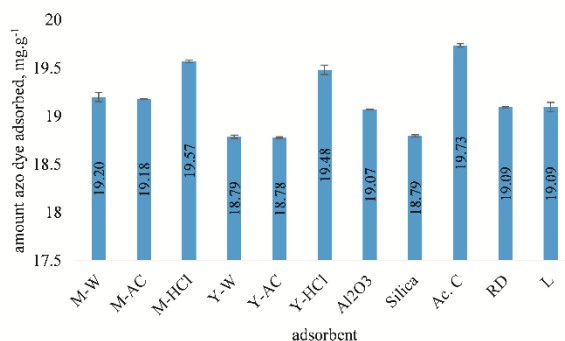


Figure 7. Pretreatment/type of adsorbent impact on the AO 7 decontamination by melissa and yarrow residues

The results confirmed that the acid-washed residues of M and Y showed the highest adsorption capacity for removal of AO 7 from water solutions. The comparison of effectiveness of adsorption with RD and L (both residues washed with deionized water) suggested that melissa and yarrow residues adsorbed higher amounts of AO 7, except the M and Y by-products washed with acetone (these residues showed the lower adsorption capacity). The highest adsorption capacity showed activated carbon (98.65% removal) but the acid-washed residues of M and Y showed very close values: 97.85% and 97.40%, respectively.

Conclusions

The data obtained for the impact of several parameters on the decontamination of AO 7 revealed the initial assumption that the melissa and yarrow residues from industrial processing could be successfully applied as cheap, renewable and nature friendly bioadsorbents. The equilibrium of the adsorption/desorption processes was established between 5th and 10th min (slight increase of the adsorption was observed until the 60th min but it was negligible) and the effectiveness of the AO 7 removal for M adsorbent was $19.39 \pm 0.12 \text{ mg.mL}^{-1}$ (96.95% efficiency) and for Y adsorbent: $19.04 \pm 0.24 \text{ mg.mL}^{-1}$ (95.20% efficiency). The pH of the medium strongly influenced the adsorption process and it was established that acidic medium (below pH 5) favors the adsorption and removal of AO 7. Both residues were pretreated (washed) with deionized water, 0.1 N HCl and acetone and successfully used for AO 7 decontamination. The data clearly indicated that acid-washed residues

were more efficient as adsorbents. A possible explanation of the observed results is protonation of the carboxylic groups from pectic polysaccharides and proteins, and by this way suppression of the repulsion between the charged groups from adsorbents and the dye (having an ionic character due to presence of sulfo-groups favors the AO 7 retention on the by-products. Additionally, at lower pH the amino-groups from proteins will bear positive charge which will favor electrostatic interactions between the adsorbents and the AO 7. Confronting the effectiveness of both dyes with well-known adsorbents (aluminum oxide, chromatographic silica gel and activated carbon) was observed adsorption rate from M and Y residues pretreated with 0.1 M hydrochloric acid higher than aluminum oxide and chromatographic silica gel and slightly lower than activated carbon, which showed the highest adsorption capacity.

Additional plus of the process for decontamination of polluted with azo dyes (AO 7) waste waters is the possibility to further degrade the adsorbent and the adsorbed dyes using the enormous capacity of higher fungi to grow on lignocellulosic substrates and to degrade substances having phenolic nature (Angelova et al. 2021; Marovska et al. 2023; Sosnicka et al. 2022). By this way, following the main “green” chemistry and circular economy perceptions full valorization of the residues from essential oil industry could be achieved, removal of pollutants from waste waters accomplished, and degradation of spent adsorbents performed and as a results of fungal growth on lignocellulosic substrate micellium-based bio-composites obtained.

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