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UTILIZATION OF INDUSTRIAL ROSE AND LAVENDER SOLID BY-PRODUCTS FOR REMOVAL OF 2-NAPHTOL ORANGE

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Abstract

Lavender (Lavandula angustifolia Mill.*) and rose (Rosa Damascena* Mill.*) industrial by-products were used as natural, biodegradable, readily available and cheap bioadsorbents to remove the azo dye 2-naphthol orange from waste waters. The influence of contact time, pH, adsorbent amount, initial dye concentration, temperature, sonication and adsorbent particle size was investigated. The acidic medium favored the adsorption and at pH 1.5, 99% efficiency (for lavender as adsorbent) was achieved. The results of the present study confirmed the successful application of essential oil industrial lavender and rose by-products as bioadsorbents for efficient removal of 2-naphtol orange from waste waters as a new method for valorization of the by-products from agricultural industry.*

Key words*: rose, lavender, by-products, 2-naphthol orange, adsorption.*

INTRODUCTION

Azo dyes are among the most widely used chemical class of dyes worldwide. They are synthesized from aromatic amines by diazotization (Crettaz et al., 2020). Azo dyes have a toxic effect on humans, as well as, on nature and aquatic life. Therefore, there is an urgent call for wastewaters containing azo dyes to be treated for their elimination or for their conversion into safer products (Benkhaya et al., 2020). Most of the dyes are mutagenic and carcinogenic, they are stable to light, temperature and biodegradation, which makes them risk-posing compounds. Therefore, effective methods to remove these substances from wastewaters are important. The methods used for the purification of the wastewaters are coagulation, flocculation, precipitation, membrane filtration, electrochemical techniques and conventional biological treatments (activated sludge). However, these techniques are not 100 percent efficient nor are they financially viable, as most of them require large land areas and are quite expensive (Kumar et al., 2011).

Adsorption is a purification process that is one of the most cost-effective methods for removing pollutants from wastewaters. It requires little space and the process is not affected by toxic chemicals. Adsorption processes also allow regeneration, recovery and recycling of the adsorbents (Nascimento et al., 2014). Besides, often by-products from agricultural industry (essential oil industry for example) could be used as natural, biodegradable, cheap and readily available adsorbents.

Hence, the aim of the present study was focused on utilization of by-products from the essential oil industry (rose and lavender solid residues) as natural, renewable and biodegradable adsorbents for removal of the azo dye 2-naphthol orange.

MATERIALS AND METHODS

Lavender (L) (bio-certified *Lavandula angustifolia* Mill., 'Sevtopolis' var.) and rose (RD) (bio-certified *Rosa Damascena* Mill.), by-products from industrial steam distillation of fresh plant material were provided by the ECOMAAT distillery (Mirkovo, region of Sofia, Bulgaria; crop 2021).

2-naphthol orange (Sodium 4-[(2-hydroxynaphthalen-1-yl)-diazenyl] benzenesulfonate) was obtained from local distributors.

The rose and lavender by-products were collected from the still after the end of industrial treatment. The solid residues were inspected for impurities and dried. The dried rose and lavender were washed with distilled water (100 g with 1600 mL water; added in portions of 400 mL) on a Buchner funnel. The residual solid mass was dried, milled and sieved. The same conditions were used for washing of the RD and L by-products with acetone, 70% ethanol and 0.1 N hydrochloric acid. For adsorption of the azo dye, fraction with particle size 50-100 µm was used.

The adsorption of 2-naphthol orange was carried out as follow: 20 mL water solution of 2-naphthol orange with the specified concentration (20, 40, 60, 80 and 100 mg/L) were added to 1 g of adsorbent in a 50 mL centrifuge tube and the tubes were put on a laboratory shaker MLW THYS 2 (VEB MLW Labortechnik Ilmenau, Germany), placed in a thermally controlled laboratory oven. The shaker was started (100 rpm) and at a specified time (2.5, 5, 10, 20, 30, 40, 60, 90, and 120 min) a centrifuged tube was removed from the shaker and the mass was filtered first through a paper filter and further through a syringe filter CA 0.45 µm (Isolab, Germany). Adsorption of the filtrate was measured at 500 nm using LLG-uniSPEC 2 UV-Vis spectrophotometer (LLG Labware, Germany) and the concentration of the remaining after the adsorption 2-naphthol orange was calculated using a calibration curve, prepared with water solutions of the dye with known concentrations.

RESULTS AND DISCUSSIONS

Influence of the contact time on the adsorption of 2-naphthol orange

The first parameter investigated was the contact time of the adsorbent with the 2-naphthol orange. This parameter determines the dye adsorption time equilibrium and is important from economic and ecological point of view (Figure 1). In the beginning of the contact of the azo dye with the adsorbent, adsorption is a fast process since there are a lot of unoccupied sites in the surface of the L and RD adsorbents. Sharp increase of the adsorbed azo dye was observed until the 30th min, after that, clearly, equilibrium was observed. At 120 min the efficiency of the adsorption at pH 7.05 was 92% for RD and 85% for L as adsorbents for 2-naphthol orange. Similar observations were made by Wu et al. (2011) investigating adsorption of 2-naphthol orange using spent brewery’s yeast. The authors found that the equilibrium of the adsorption was reached after 20-30 min contact time.

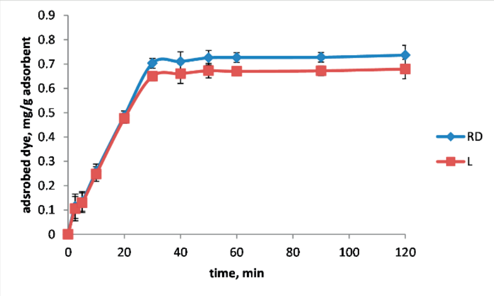

Figure 1. Influence of the contact time on the adsorption of 2-naphthol orange (initial concentration of the azo dye: 0.8 mg/20 mL; pH: 7.05; amount of the adsorbent: 1 g; temperature: 20ºC; shaking at 100 rpm)

Influence of the pH of the medium on the adsorption of 2-naphthol orange

Furthermore, the effect of the pH of the medium was investigated (Figure 2). The acidic medium favored the adsorption process and the highest effectiveness of the removal for both adsorbents was achieved at pH 3.5. At pH 1.05, however, the L residue was able to eliminate 99% 2-naphthol orange. At pH 10.75 almost no adsorption of 2-naphthol orange was observed. These results are supported by the findings of Wu et al. (2011) and Pelosi et al. (2013) investigating adsorption of 2-naphthol orange on waste biomasses. However, in the work of Wu et al. (2011) the effectiveness of the adsorption lowered significantly after pH was raised above 5. In our case both adsorbents RD and L could be utilized at pH levels up to 7. This observation is important because it is much easier to operate industrially at neutral pH than at acidic medium. Besides, further it will be necessary to neutralize the spent adsorbent and also treatment of the solution will be necessary.

The effectiveness at lower pH might be related to the net charge of the adsorbents. The main functional groups which could contribute to the adsorption are carboxyl and hydroxyl groups (Hamzeh et al., 2012). At lower pH medium these groups will be protonated and attraction will favor retention of the 2-naphthol orange. Due to its anionic character, at higher pH (when the carboxyl groups will not be protonated) electrostatic repulsion will lower the effectiveness of the adsorption.

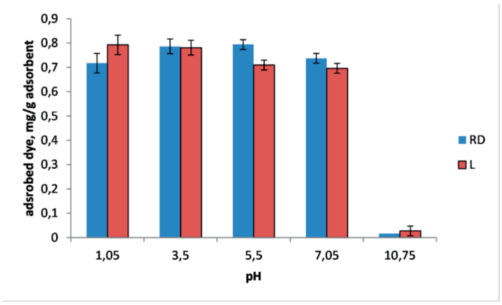

Figure 2. Influence of the pH on the adsorption of 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; amount of the adsorbent: 1 g; temperature: 20ºC; shaking at 100 rpm)

Influence of the amount of the adsorbent/re-adsorption on the adsorption of 2-naphthol orange

The amount of adsorbent plays important role and usually contributes to the better effectiveness in the percentage removal of the pollutant. The best results were achieved (Figure 3) using 1.5 and 2 g RD adsorbent (single adsorption; almost 99% removal was achieved). For the L residue these amounts lead to retention of the solution and it was impossible to separate the purified water.

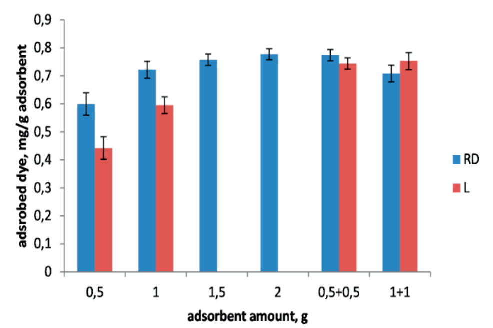

Figure 3. Influence of the amount of the adsorbent/re-adsorption on the adsorption of 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; pH: 7.05; temperature: 20ºC; shaking at 100 rpm)

Consecutive adsorption was also tested and it was found that for both adsorbents doses of 0.5+0.5 g and 1+1 g adsorbents were highly effective. One of the problems arising using consecutive adsorption was related to the higher water retention capacity of the RD and L, having highly hydrophilic character. At doses of 1.5+1.5 g adsorbents no water phase could be obtained after adsorption.

Influence of the initial concentration of the 2-naphthol orange on the adsorption

At all the investigated dye concentrations (0.02 to 0.1 mg/mL) the effectiveness of the adsorption achieved was around 90%. The highest percentage (92.74%) of adsorption of 2-naphthol orange (at 0.04 mg/mL concentration) has the RD adsorbent (Figure 4). This might suggest that the capacity of the adsorbents RD and L is much higher than 0.1 mg/mL per 1 g adsorbent.

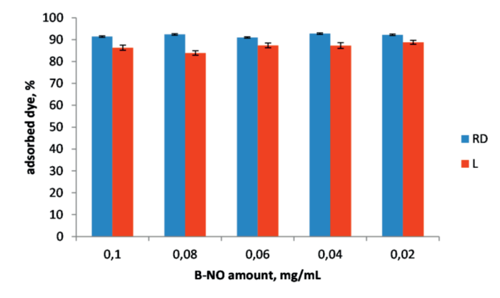

Figure 4. Influence of the concentration of the 2-naphthol orange on the adsorption (contact time 40 min; amount of the adsorbent: 1g; pH: 7.05; temperature: 20ºC; shaking at 100 rpm)

Influence of the temperature on the adsorption of 2-naphthol orange

In general the effect of temperatures above 20°C was negative on the effectiveness of adsorption for both adsorbents and this was more clearly expressed for L (Figure 5). This effect might be due to the increased rate of desorption with increase of the temperature.

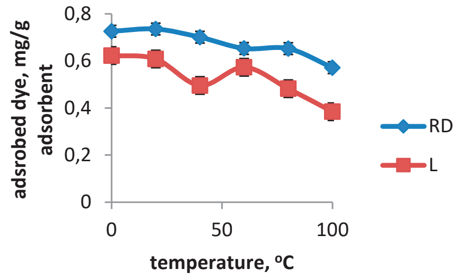

Figure 5. Influence of the temperature on the adsorption of the 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; amount of the adsorbent: 1 g; pH: 7.05; shaking at 100 rpm)

Influence of the particle size of the adsorbent on the adsorption of the 2-naphthol orange

In the next experiments the influence of the particle size of the adsorbents on the adsorption was investigated. Results presented in Figure 6 clearly demonstrated that for both adsorbents particles with a size of 50 μм or below had adsorbed most effectively the azo dye. This result is not surprising having in mind that the lower the particle size the more active surface the adsorbent will have.

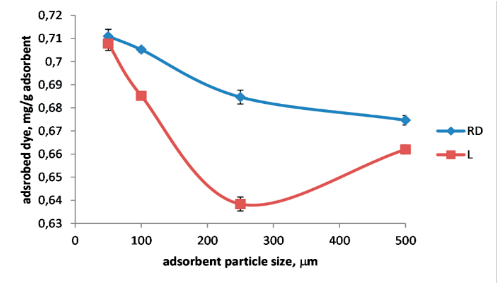

Figure 6. Influence of the particle size of the adsorbent on the adsorption of the 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; amount of the adsorbent: 1 g; pH: 7.05; shaking at 100 rpm)

Influence of the type of the adsorbent on the adsorption of the 2-naphthol orange

In the following experiments the RD and L were compared with several known adsorbents: activated carbon, Al_2O_3 and silicagel (Figure 7). The best results for adsorption effectiveness showed the activated carbon. RD and L showed better adsorption capacity than Al_2O_3 and silicagel and the percentage of removal of 2-naphthol orange was closer to that of the activated carbon. The type of the initial pretreatment of the rose and lavender by-products was also assessed. Both by-products were washed with 70% ethanol, acetone and 0.1 N hydrochloric acid (HCl), dried and used as adsorbents. The results suggested that acid washing was beneficial to the applicability of the residues as adsorbents. The best adsorption effectiveness showed both acid-washed rose and lavender adsorbents, as L_Res_AE adsorbed 0.7918 mg/mL of 0.8 mg/mL 2-naphthol orange (almost 99% removal of the dye). This corresponds well with the results obtained for the influence of the pH on the adsorption of the 2-naphthol orange (Hamzeh et al., 2012).

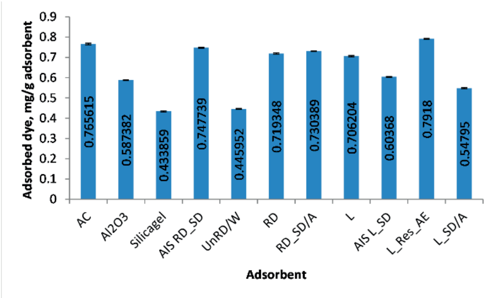

Figure 7. Influence of the type of the adsorbent on the adsorption of the 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; amount of the adsorbent: 1 g; pH: 7.05; shaking at 100 rpm). AC - active carbon; Al_2O_3; Silicagel; AIS RD_SD - rose by products washed with 70% ethanol; UnRD/W - dried rose petals (non-distilled) washed with distilled water; RD - steam-distilled rose by-products washed with distilled water; RD_SD/A - rose by products washed with acetone; L - steam-distilled lavender by-products washed with distilled water; AIS L_SD - lavender by-products washed with 70% ethanol; L_Res_AE - steam-distilled lavender by-products washed with 0.1 N HCl; L_SD/A - lavender by products washed with acetone

Influence of the ultrasound treatment on the adsorption of the 2-naphthol orange

Ultrasound treatment has gained popularity during the recent years with its simplicity and effectiveness for many industrial applications (Slavov et al., 2019). Ultrasound could be successfully applied for adsorption/desorption purification processes in the food industry (Wu et al., 2018), pollutant removal (Hamdaoui, et al., 2003), etc. Hence, in the next experiments the influence of the sonication on the removal of 2-naphthol orange was studied (Figure 8).

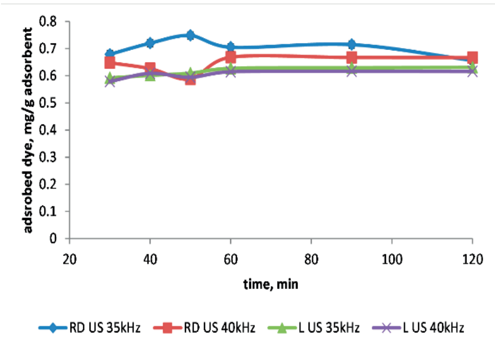

Figure 8. Influence of the ultrasound treatment on the adsorption of the 2-naphthol orange (contact time 40 min; initial concentration of the azo dye: 0.8 mg/20 mL; amount of the adsorbent: 1 g; pH: 7.05)

Two treatments - at 35 kHz and at 40 kHz frequency were investigated. It could be seen that equilibrium was established after around 20-30 min and the percentage removal was similar to the experiments for the contact time (without sonication) (Figure 1). This suggested that at the experimental conditions sonication did not improved significantly the removal by adsorption of the 2-naphthol orange. Similar observations were made by Hamdaoui et al. (2003) while investigating adsorption/ desorption process of *p*-chlorophenol on granular activated carbon. One possible explanation of the results obtained was that along with the adsorption intensification from sonication, the reverse process of desorption also occurred with time, when the adsorbent had already adsorbed its maximum azo dye.
The results from the experiments suggested that RD and L by-products could be successfully applied as a bioadsorbent for removal of the azo dye 2-naphthol orange from water solutions. The residues generated after adsorption of 2-naphthol orange could be used as a substrate for further higher fungi degradation and production of mycelium based biocomposites (Angelova et al., 2021). Due to the phenolic nature of the 2-naphthol orange the higher fungi, able to produce lignocellulosic enzyme complexes, could successfully degrade the azo dye and by this way completely eliminate the hazardous threat for the nature.

CONCLUSIONS

The present study explored the application of two industrially generated by-products of the essential oil rose and lavender industry. The by-products are cheap, renewable, biodegradable and natural substances, which could be successfully applied for biosorption of organic pollutants, such as azo dyes. The influence of contact time, pH, amount of the adsorbent and 2-naphthol orange, particle size, temperature, initial pretreatment of the adsorbent and mechanical treatment were investigated. It was found that equilibrium was established after 20-30 min contact time, and that the lower pH favors the adsorption process. The increase of the temperature influenced negatively the removal of 2-naphthol orange and the best results were obtained at temperatures below 20°C. The adsorbents' particle size below 50 μм showed the best results for adsorption effectiveness. Acid washing (with 0.1 N HCl) as a pretreatment leads to the best results for removal of 2-naphthol orange from the medium. The resulted adsorbents had adsorption capacity higher than that of activated carbon as a well-known commercially available adsorbent. The best adsorption effectiveness showed both acid-washed rose and lavender adsorbents, as lavender acid washed by-product adsorbed 0.7918 mg/mL of 0.8 mg/mL 2-naphthol orange (almost 99% removal of the dye).

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