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# Decontamination of waste waters containing azo dye β-naphthol orange with residues from essential oil industry – common sage (*Salvia officinalis* L.) and yellow hornpoppy (*Glaucium flavum* Crantz)

I. Hambarliyska[1]*, A. Bylianova[1], B. Bozadjiev[2], A. Slavov[1]

*[1]Department of Organic and Inorganic Chemistry, Technological Faculty, University of Food Technologies, 26 Maritsa Blvd., Plovdiv 4000, Bulgaria.*

*[2]Department Technology of Grain, Fodder, Bakery and Confectionery Products, Technological Faculty, University of Food Technologies, 26 Maritsa Blvd., Plovdiv 4000, Bulgaria*

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Waste waters containing the azo dye β-naphthol orange (βNO) were subjected to purification by adsorption using common sage (CS) and yellow hornpoppy (YH) residues from essential oil industry. The preliminary characteristic of the biomasses suggested that they contain 71.85±1.74% (CS) and 64.06±0.46% (YH) total dietary fibers (DF), and 6.59±0.28% and 5.44±0.86% soluble DF, respectively. The adsorption equilibrium was reached around the 20th min (1 g adsorbent; 20 mL, 1 mg/mL dye in water), and the amount of adsorbed azo dye was 19.58±0.12 mg (0.64 mg/mL from 1 mg/mL – 63.52% efficiency) for CS and 19.55±0.24 mg/mL (0.71 mg/mL from 1 mg/mL – 71.24% efficiency) for YH. Preliminary washing of the residues with 0.1 N HCl increased their decontamination abilities. At pH 1.1 the βNO removal was above 99±0.1% for both CS and YH. Comparison of the removal efficiency of CS and YH with aluminum oxide, silica gel, activated carbon, *Rosa damascena* Mill. (RD), *Lavandula angustifolia* L. (lavender, L), *Melissa officinalis* L. (melissa (M)) and *Achillea millefolium* L. (yarrow (Y)) wastes, suggested similar decontamination abilities for RD, L, M and Y (55-79%), while activated carbon showed 90% adsorption. The present study suggests that CS and YH wastes are able to remove βNO from water solutions with 56.75% and 64.16% efficiency, respectively.

**Keywords**: β-naphthol orange, azo dye, common sage (*Salvia officinalis* L.), yellow hornpoppy (*Glaucium flavum* Crantz), bio-adsorption.

## INTRODUCTION

Azo dyes are among the most widely used organic pigments with wide applications in textile and food industries [1]. Some of the azo dyes might be toxic to living organisms. Exposure to light, mild temperatures and microorganisms' action brake down their molecules at a slow pace or not at all, making the azo dyes hazardous substances. Therefore, developing and applying functional techniques for decontamination of wastewaters containing azo dyes is a must [2].

β-Naphthol orange (βNO) is used for dyeing silk, polyamide and wool textile, paper products, toner preparations, leather goods, hairs cosmetics, and in staining for scientific purposes [3]. Numerous processes, such as microbial decay, exposure to oxidizing agents (including light), and adsorption [4] could be found in the literature and in practice. The latter method could be considered as the most used for βNO removal. Copious compounds and matters were investigated as adsorbents [4-6] as waste materials from various industries (electricity generation, agriculture, timber, food, etc.) showed promising potential [7-11]. However, in the literature, to the best of our knowledge, no data could be found on the application of common sage (CS) and yellow hornpoppy (YH) industrial wastes for the purification of waters contaminated with azo dyes, such as βNO. For this reason, the present study focused on the utilization of CS and YH biomasses as adsorbents for βNO removal from its water solutions.

## MATERIALS AND METHODS

### *Materials*

The common sage (*Salvia officinalis* L.) biomass, resulting from industrial steam distillation of bio-certified fresh plants, was supplied by Mirkovo distillery (Mirkovo, Sofia region, Bulgaria, 2024 harvest). The yellow hornpoppy (*Glaucium flavum* Crantz) residue (after extraction of the raw material with methanol containing 35% $H_2SO_4$ for obtaining of glaucine) was donated by Zelenikovo distillery (Zelenikovo, Brezovo region, Bulgaria, 2024). βNO (4-(2-hydroxy-1-naphthylazo) benzenesulfonic acid sodium salt) was obtained from Merck (Germany).

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* To whom all correspondence should be sent:
Email: *i_hambarliyska@uft-plovdiv.bg*

### Methods

The CS and YH biomasses were roughly chopped using a garden shredder and then finely milled with a laboratory milling machine (average particle size of 483.9±2.6 μm). The milled residues were dried in a laboratory thermostatic drier Diterm (Robotika, Velingrad, Bulgaria) at 60 °C for 48 h. The biomasses were washed with deionized water, acetone, 0.1 N HCl, and 0.1 N NaOH, as described in [12].

1) *Contact time of the adsorbent with βNO*. The βNO removal was carried out as described in [12]. After filtration of the solutions the adsorption of the non-absorbed dye was measured at 500 nm (LLG-uniSPEC 2, LLG Labware, Germany). The concentration of the unabsorbed *βNO* was determined using a calibration curve, plotted with dye's aqueous solutions with specified concentrations.

2) *Solutions' pH sway on βNO removal.* Solutions of βNO (1 mg/L) in several solvents were prepared: 1. *pH 1.*10 – 0.1 M sulfuric acid 2. *pH 3.55* – deionized water; 3. *pH 5.30* – 50 mM citrate buffer; 4. *pH 8.*10 – 50 mM phosphate buffer; 5. *pH 12.*90 – 0.1 N sodium hydroxide. The experiments were performed as described above (point 1). The conditions were: time 40 min, βNO concentration: 1 mg/mL (20 mL), adsorbent mass: 1 g; room temperature (20 °C), and shaking rate – 100 rpm. After the end of the specified time, filtration and determinations were performed as described in point 1).

3) *Temperature influence on βNO removal.* Temperature effect on βNO removal was investigated at 0, 20, 40, 60, 80 and 100 °C. The conditions were: time 40 min, βNO concentration: 1 mg/mL (20 mL), adsorbent mass: 1 g; pH: 3.55; shaking rate – 100 rpm. After the end of the specified time, filtration and determinations were performed as described in point 1).

4*) Initial washing / adsorbent influence on βNO removal*. The impact of the initial washing of the raw material or adsorbent on βNO removal was performed with activated carbon (Himtex Ltd., Dimitrovgrad, Bulgaria), $Al_2O_3$ (Merck, Germany) and silica gel (Reanal, Budapest, Hungary), biomasses from lavender (*Lavandula angustifolia* L.), melissa (*Melissa officinalis* L.), and yarrow (*Achillea millefolium* L.), resulting after industrial steam distillation (denoted as L, M and Y, respectively); *Rosa damascena* Mill. biomass, resulting from steam-water distillation (RD); L, M, Y and RD biomasses were obtained from Zelenikovo distillery (2022 harvests). The conditions were: time 40 min, βNO concentration: 1 mg/mL (20 mL), room temperature (20 °C), adsorbent mass: 1 g; pH: 3.55; shaking rate – 100 rpm. After the end of the specified time, filtration and determinations were performed as described in point 1).

5) *βNO concentration influence*. Solutions of βNO in water with 0.125, 0.25, 0.5, 1.0 and 2.0 mg/mL concentrations were subjected to adsorption with CS and YH: time 40 min, 20 °C, adsorbent mass: 1 g; pH: 3.55; shaking rate – 100 rpm. After the end of the specified time, filtration and determinations were performed as described in point 1).

The moisture content of the dried CS and YH residues was determined using analytical balance Kern DAB 100-3 (Kern&Sohn Gmbh, Balingen, Germany). The protein quantities were determined by the Kjeldahl method (MultiKjel K-365 – Büchi, Switzerland) using 6.25 nitrogen multiplication factor. The PUC and DE of the biomasses were determined as described in [12]. The dietary fibers analyses were performed with K-TDFR-100A (Megazyme, Ireland).

### Statistical analysis

The experimental data (three replicates) are presented as mean value ± standard deviation. For analysis one-way ANOVA test (Tukey's post hoc test; $p < 0.05$) was used with Microsoft Excel 2013 (additional XL Toolbox NG module installed).

## RESULTS AND DISCUSSION

### Preliminary characteristics of CS and YH residues

The analyses of the CS and YH residues revealed that they were rich in lignocellulosic material (Table 1). The amounts of TDF determined for CS and YH were 64.06±0.46% and 71.85±1.74%, respectively and the IDF fraction was predominating – 57.47±0.46% for CS and 66.41±1.74% for YH. The protein amount determined for CS was 12.34±1.14% and 8.66±0.92% for YH biomass. The CS residue (8.03±0.40%) had two times higher ash content than YH (3.31±0.16%). One possible explanation could be the difference in their processing – the YH raw material was extracted with methanol containing 35% sulfuric acid and this extractant could remove a large part of the inorganic matter. The moisture content of the biomass was 10.11±0.15% and 10.95±0.27% for YH and CS, respectively. The PUC, commonly referring to pectins in the plant matrix, differed significantly for both residues – 10.62±0.20% for YH and 3.83±0.20% for CS.

**Table 1.** General characteristics of sage and yellow poppy residues: soluble (SDF), insoluble (IDF) and total dietary fiber (TDF), protein, ash, moisture, degree of esterification (DE) and polyuronide content (PUC)

| | DF | | | Protein, % | Ash, % | Moisture, % | DE, % | PUC, % |
|---|---|---|---|---|---|---|---|---|
| | TDF, % | IDF, % | SDF, % | | | | | |
| CS | 64.06±0.46$^{b}$ | 57.47±0.46$^{b}$ | 6.59±0.28$^{a}$ | 12.34±1.14$^{a}$ | 8.03±0.40$^{a}$ | 10.31±0.12$^{a}$ | 69.89±0.16$^{a}$ | 3.83±0.20$^{b}$ |
| YH | 71.85±1.74$^{a}$ | 66.41±1.74$^{a}$ | 5.44±0.86$^{a}$ | 8.66±0.92$^{b}$ | 3.31±0.16$^{b}$ | 9.47±0.14$^{a}$ | 62.33±1.31$^{b}$ | 10.62±0.20$^{a}$ |

Results are presented as the mean of three measurements; $^{a,b}$ Different letters in columns indicate statistically different values (Tuckey's HSD test, $p < 0.05$).

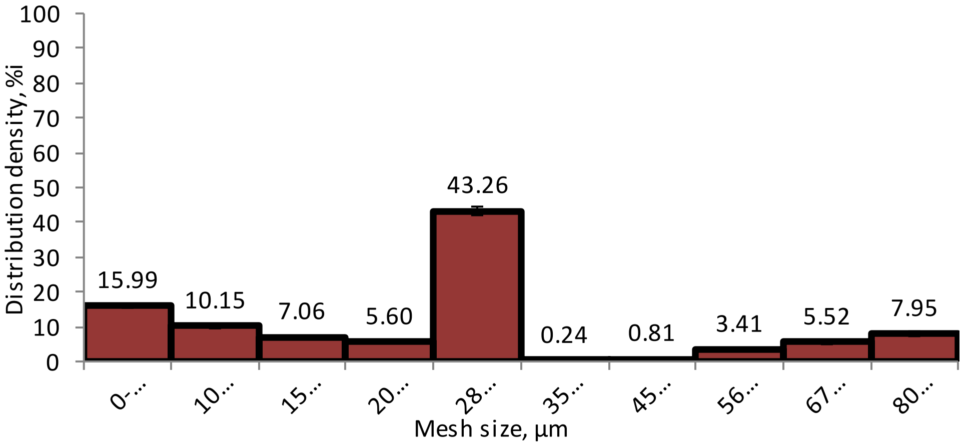

**Figure 1.** Distribution density pattern of the CS and YH residues

This could also be explained with the different industrial processing of the plant material, as it is known that alcoholic solutions preserve extraction of polysaccharides to a large extent. Figure 1 presents information from the mesh size analyses of CS and YH. The average particle size of the residues was 483.9±2.6 µm and the dominating fraction was 280-355 µm (43.26%).

*Contact time influence on βNO adsorption*

The CS and YH residues were pretreated with four solvents: deionized water, 0.1 N HCl acetone and 0.1 N NaOH. These washings intended removal of low-molecular organic and inorganic matters from the residues and also activation / deactivation of the functional groups of compounds present in the plant materials – mostly carboxyl (pectins and proteins) and amino groups (proteins).

Adsorption kinetics of βNO removal by the residues was initially explored. The experimental observations are presented in Figure 2 for CS and Figure 3 for YH residues. Adsorption is based on physical and chemical interactions of the adsorbent with the substances in the solution. The predominating functional groups in the adsorbent and the compounds adsorbed play a vital role and determine the effectiveness of the process. These interactions are stronger and adsorption is faster in the beginning because of the availability of a lot of unoccupied groups on the surface of the adsorbent [9].

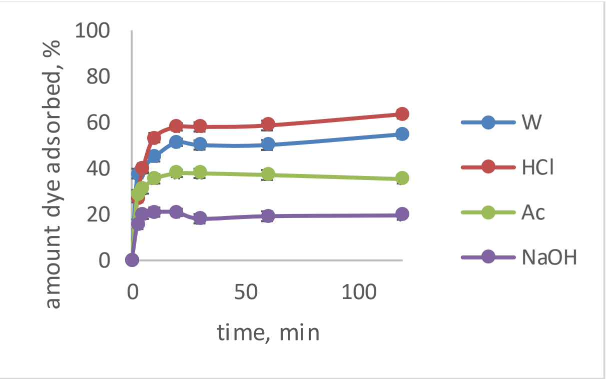

**Figure 2.** Contact time influence on βNO adsorption by CS residue washed with deionized water (W), 0.1 M HCl (HCl), acetone (Ac) and 0.1 M NaOH (NaOH)

Equilibrium is established when adsorbent's groups are taken by the adsorbed compounds and equilibrium concentration is reached. Our observations suggested that equilibrium for CS and YH was reached between 10th and 20th min. For CS residue washed with 0.1 N HCl effectiveness of removal around 60% was observed while for other the adsorbent it was lower. For YH residues washed with deionized water (W), 0.1 M HCl (HCl) and acetone (Ac) the removal effectiveness exceeded 60%. For both residues washed with 0.1 N NaOH the effectiveness was lower: between 15-20%.

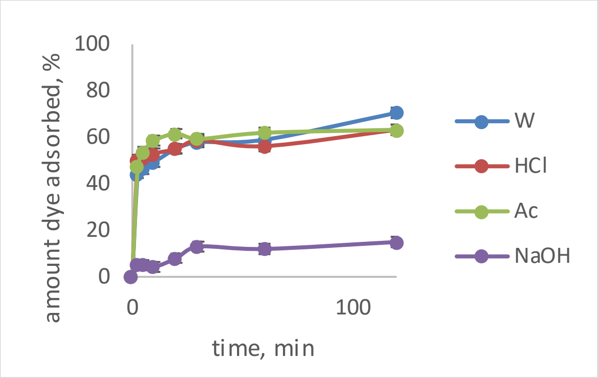

**Figure 3.** Contact time influence on βNO adsorption by YH residue washed with deionized water (W), 0.1 M HCl (HCl), acetone (Ac) and 0.1 M NaOH (NaOH)

### *Influence of pH on βNO removal*

In the next experiments, because of the observations from previous section, the pH influence on βNO removal was explored. The adsorption process was investigated with five solutions having from high acidity – 1.10 to highly basic pH – 12.90 (Figure 4 – CS residue; Figure 5 – YH residue). The data clearly showed that lower pH (5 or less) increases adsorption effectiveness for both residues. The highest percentage of removed βNO was observed at pH 1.10 – almost 90% for CS and around 80% for YH.

In any cases, above pH 7 adsorption effectiveness of the CS and YH residues dropped down below 50% and for YH pretreated with NaOH it was the lowest one. Similar observations and conclusions were made in the studies [9, 13, 14] focusing on βNO removal using rose and lavender (residues from industry for essential oil production), brewery spent yeasts, and melissa and yarrow wastes (also from industry for essential oil production), respectively. Because βNO (as a salt) is a charged compound, lowering the pH would result in less electrostatic repulsion between the dye and plant matrices (pectins and proteins could be regarded as the biopolymers having the highest amount of charged groups – carboxyl and amino).

### *Temperature influence on βNO removal*

The best results for βNO adsorption were observed at lower temperatures: 20 or below. At 40°C or above a trend for lowering the capacity was clearly observed (Figures 6 and 7). CS residues washed with water and 0.1 N HCl showed the highest effectiveness at 20 °C and for YH the residue pretreated with acetone showed the highest effectiveness at 20 °C (above 80%) and at 4 °C (above 70%). Comparably, Marovska *et al.* [9] and Hambarliyska *et al.* [14] showed that temperature increase lowered the adsorption rate of βNO on rose and lavender (steam-water and steam distilled) residues and melissa and yarrow biomass (steam distilled), respectively.

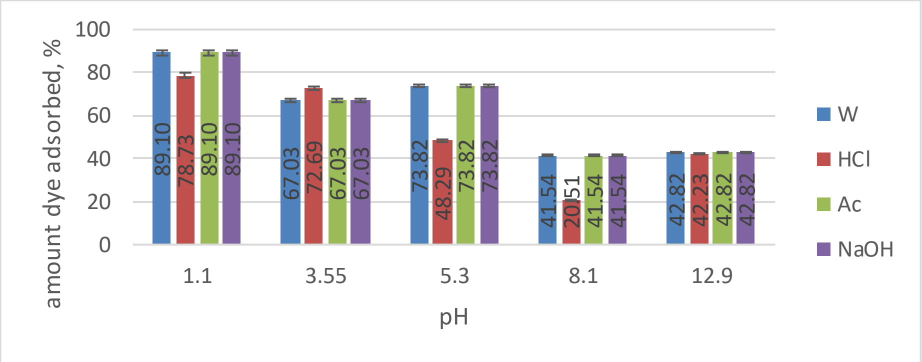

**Figure 4**. pH influence on βNO removal by CS residue

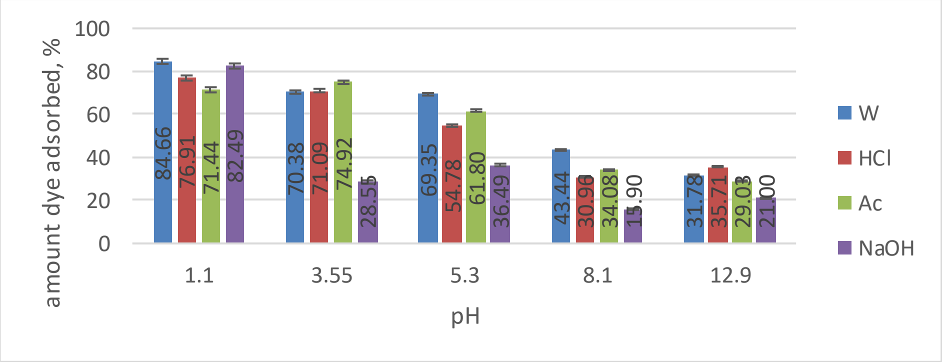

**Figure 5.** pH influence on βNO removal by YH residue

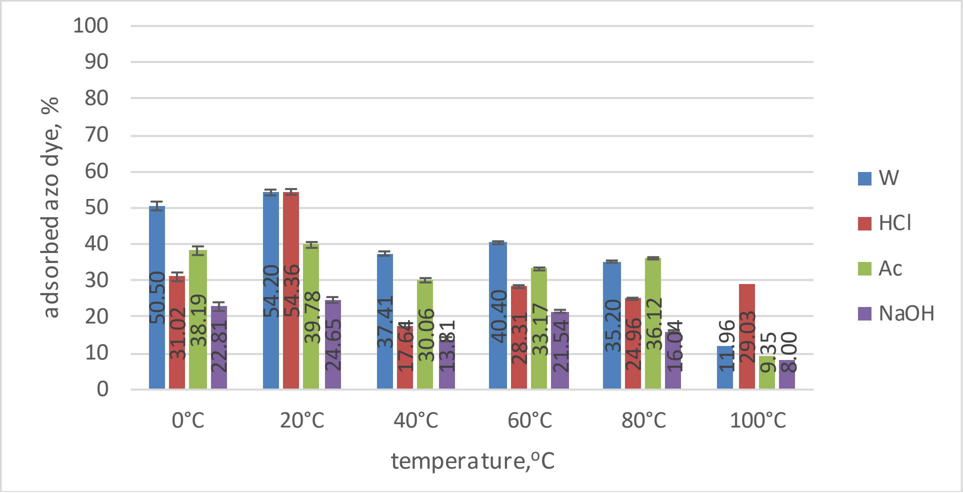

**Figure 6.** Temperature influence on βNO removal by CS residue

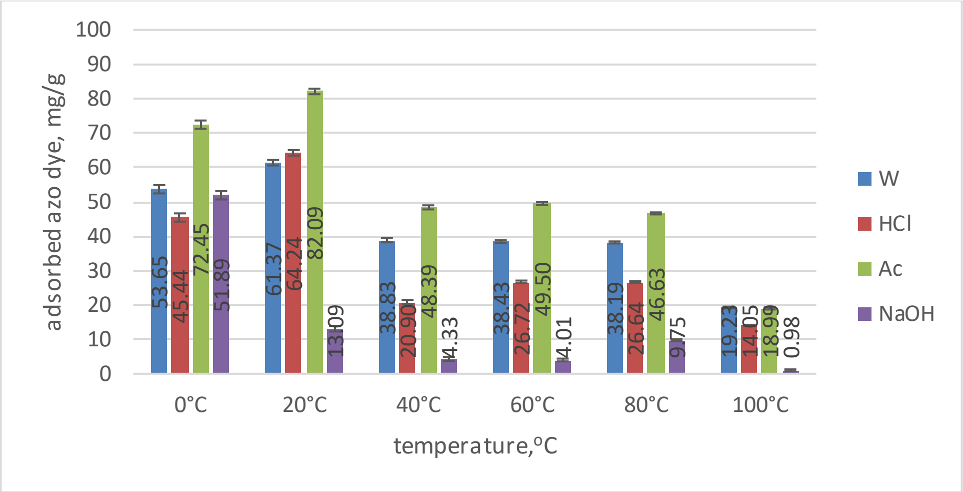

**Figure 7.** Temperature influence on βNO removal by YH residue

This trend for unfavorable influence and decrease in adsorption rate might be explained with increasing the desorption rate when increasing the temperature.

### *Initial treatment / adsorbent influence on βNO removal*

Furthermore, juxtaposition of the adsorption of βNO by CS and YH (residues washed with water) and other materials (three substances used industrially: $Al_2O_3$, silica gel (chromatographic), activated carbon, and biomasses from industrial distillation of rose (RD), lavender (L), melissa (M), and yarrow (Y) was carried out (Figure 8). The data suggest that YH (water washed) residue showed a potent effectiveness for βNO removal (around 65%). Only activated carbon, M and Y residues (pretreated with 0.1 N HCl) showed better performance (almost 90%, 80% and 75%, respectively). Juxtaposition of effectiveness of common sage with rose and lavender (all pretreated with water) revealed similar adsorption capacity with slightly better performance by CS_W. Close results were demonstrated by Hambarliyska *et al.* [14] investigating the removal of βNO with residues from melissa and yarrow and Marovska *et al.* [9] researching adsorption of βNO with rose and lavender post-distillation biomasses.

### *Influence of βNO initial concentration on removal effectiveness*

Further, the removal of βNO from its solutions with different concentrations was explored (Figure 9). For all investigated concentrations of βNO (2, 1, 0.5, 0.25, and 0.125 mg/mL) the CS and YH residues (initially pretreated with water) were able to remove aboe 50% of the azo dye. The highest effectiveness was observed for 0.125 and 0.25 mg/mL concentrations – 80% and almost 70% removal, respectively. Both adsorbents showed similar adsorption effectiveness, the negligible differences being within the limit of statistical insignificance.

Confronting the results of the present study with those obtained by Marovska and Slavov [12] who investigated the removal of βNO with rose and lavender biomass, it could be concluded that CS and YH residues showed slightly lower adsorption effectiveness.

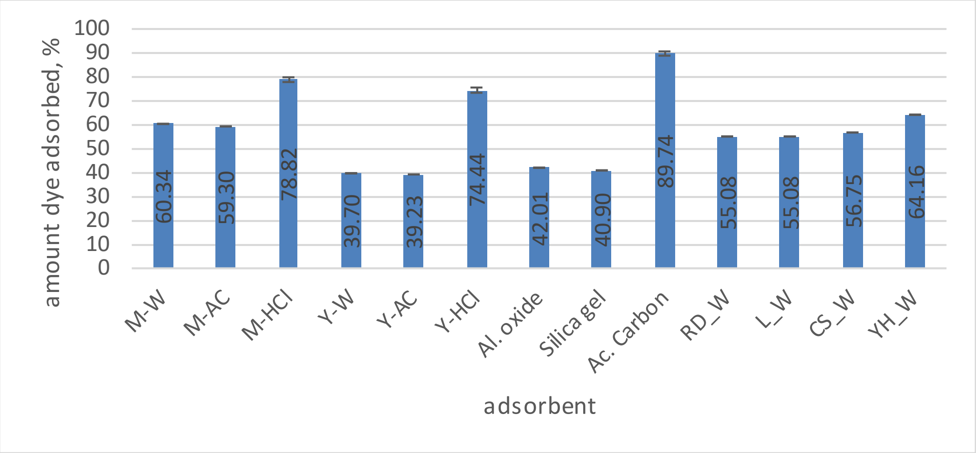

**Figure 8.** Juxtaposition of initial treatment / adsorbent influence on the βNO adsorption

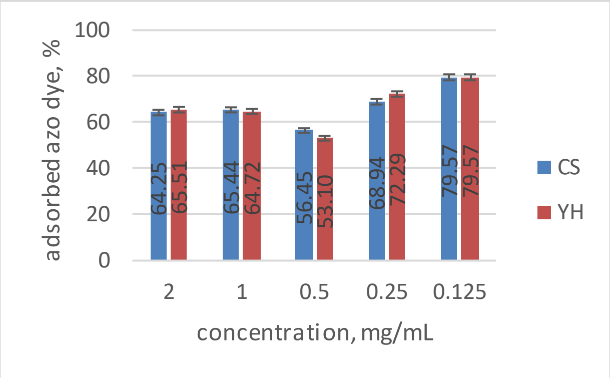

**Figure 9.** Influence of initial concentration of βNO on its removal by CS and YH. βNO below 0.5 mg/mL.

## CONCLUSIONS

The present study focused on the adsorption of azo dye βNO with two residues from the industry of essential oil production, namely common sage and yellow hornpoppy (initially pretreated with four solvents), which showed a promising potential for waste waters purification. Residues washed with 0.1 N HCl demonstrated the highest adsorption capacity for βNO removal. The equipoise state of adsorption was reached between 10th and 20th min. The pH was the predominating factor affecting the adsorption rate and below pH 5 higher efficiency was observed. Juxtaposition of the effectiveness of CS and YH residues (water-washed) with that of several adsorbents ($Al_2O_3$, silica gel, activated carbon, and rose, lavender, melissa and yarrow post-distillation biomasses) lead to the conclusion that YH showed better adsorption effectiveness than CS. The optimal conditions for βNO removal could be summarized as follows: pH below 3, initial pretreatment of the residues with dilute acids, temperatures below 20 °C, contact time 30 min, and initial concentration of βNO below 0.5 mg/mL.

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