**Nitrogen-modified nanoporous activated carbon from eucalyptus leaves for ultrasound-assisted removal of basic dyes using derivative spectrophotometric method**

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**Dear Respected Chief Editor of “Journal of the Serbian Chemical Society”**

Thank you for considering our manuscript. We thank the reviewer for his/her helpful comments and suggestions which significantly improved our paper. We have made all the necessary changes according to the referees' recommendations where it was found appropriate. Moreover, we increased the quality of the figures. We hope that it will meet with your considerations.

Sincerely yours,

**Aisan Khaligh**

**Response to Reviewer**

All the referee's comments are applied as follows:

**1)** Section: The analysis of the single solutions and simultaneous mixtures.… Line 331zero order adsorption spectrum of BY13 dye in binary solution overlapped. It should be written that spectra of BY13 and BR46 overlapped.

With thanks, it should be noted that only the spectrum of BY13 overlapped in binary solution and not both of the dyes. Therefore this sentence was corrected as below:

The absorption spectrum of BY13 dye in binary solution overlapped.

**2)** Please, comment on the reason for which the first derivative was used only for determining BY13 in binary solution? (unlike in Ref. 2. where both overlapping spectra were treated) Why did the authors keep the wavelength of 530 nm (Fig. 3a), instead of 490 nm (1DBY13) for example (where the contribution of B13 starts to be zero, Fig. 3b), for determination of BR46
concentration? What would have happened if concentration of B46 had been determined at 490 nm, using the first derivative, instead of at 530 nm using zero spectra?

With thanks, as can be seen in Figs. 2 a-b, the absorbance band of BY13 dye (λmax= 411 nm) in single solution is lower than its absorbance band in binary solution. Therefore, the absorption spectrum of BY13 dye in binary solution overlapped. On the other word, we cannot exactly determine the BY13 concentration of binary dye solution at the related λmax.. This problem was solved using derivative spectrophotometric method. The first-order derivative spectrophotometry was used for the analysis of BY13 dye in the binary dye solution at 385 nm, because at this wavelength the absorbance of the other dye (BR46) was zero and there was not any interference for this measurement. On the other hand, the absorbance bands of BR46 dye (λmax= 531nm) with concentration of 10 mg L-1 matched in single and binary dye solutions, therefore there was not any overlapping for determination of BR46 dye in binary solution. BR46 can easily be determined at λmax= 531nm without any derivative.

**3)** Line 333. For the clarity, the sentence should be rephrased: The first-order derivative spectrophotometry was used for the analysis of BY13 dye in the binary dye solution at 385 nm…..-The first-order derivative spectrophotometry (Fig. 3b) showed that the wavelength of 385 nm should be used for the analysis of BY13 in the binary dye solution, where the absorbance of BR46 is zero.

With thanks, the necessary revision has been done accordingly in the main text.

**4)** Denote in Fig. 3b the point where 1DB46=0
With thanks, the necessary revision has been done accordingly. Please see Fig. 2b of revised manuscript, this point has been denoted by black spot.

**5)** Experimental-Spectrophotometry with zero and derivative methods applied should be presented separately from Ultrasound-assisted procedure

With thanks, this work is a continuous study and the main aim was to study the adsorption of binary dye solution using NOAC adsorbent. Derivative spectrometry method was applied to measure the dye concentration due to the overlapping problem. Therefore, the separate present of the derivative spectrometry method from US-assisted procedure may not be useful and results in misunderstanding. This is similar to the previous studies:

1. N.M. Mahmoodi, R. Salehi, M. Arami. Desalination. 272 (2011) 187.

2. M. Ghaedi, S. Hajati, B. Barazesh, F. Karimi, G. Ghezelbash. J. Ind. Eng. Chem. 19 (2013) 227.

3. S. Hajati, M. Ghaedi, F. Karimi, B. Barazesh, R. Sahraei, A. Daneshfar. J. Ind. Eng. Chem. 20 (2014) 564.

4. M. Ghaedi, S. Hajati, M. Zare, S.S. Jaberi. Rsc Advances. 5 (2015) 38939.

**6)** Line 223. The sentences:  In binary solutions….and The optimal …should be deleted as they represent findings, and are presented later in Results and discussion.

With thanks, the necessary revision has been done accordingly in the main text.

**7)** Lines 340 and 341: Calibration range should be given

With thanks, the necessary revision has been done accordingly in the main text. Moreover, there was a typo in calibration equations which has been corrected.

**8)** Delete BY28 from all figure legends and from the text!!! If I clearly understood, basic dyes BY13 and BR46 were used and not BY28. Accordingly, a mistake in the last line of Table V, leads to a question: what was actually analyzed in this study: BY13 or BY28?

With thanks, the necessary revision has been done accordingly in the main text. The studied dyes were BR46 and BY13.

**9)** Only SI units should be kept, delete all ppm from Figures.

With thanks, the necessary revision has been done accordingly in the Fig. 2 and Fig. S-3.

**10)** I suggest Fig. 4 to be also transferred to Supplementary and presented together with related Table S-III.
With thanks, the necessary change has been done accordingly. Figure 4 was transferred to Supplementary Material (see Fig. S-3).

**11)** Data on kinetics and isotherm studies are lacking, only modeling is given
(Tables V-VI ). They have to be included at least in the Supporting
Material. For the sake of clarity, only present the best fit.

With thanks, the isotherm and kinetics plots have been given in the supplementary material (see Fig. S-4) and the corresponding data are presented here for your review (Please see Tables 1-3):

**Table 1.** Langmuir isotherm data for removal of BY13 and BR46 by NOAC from single solutions (Sample volume 100 mL, pH=9, *m*=30 mg, *t*=8 min, *T*=25 ºC).

|  |  |  |  |
| --- | --- | --- | --- |
| System | Dye | *C0* /mg L-1  | Langmuir |
| *Ce* /mg L-1 | *R/**%* | *qe/*mg g-1 | *Ce/qe* |
| Single | BY | 200 | 3 | 98.5 | 656.6667 | 0.004569 |
| 250 | 12.25 | 95.1 | 792.5 | 0.015457 |
| 300 | 25.5 | 91.5 | 915 | 0.027869 |
| 350 | 42 | 88 | 1026.667 | 0.040909 |
| 400 | 64 | 84 | 1120 | 0.057143 |
| Single | BR | 200 | 3.6 | 98.2 | 654.6667 | 0.005499 |
| 250 | 15.25 | 93.9 | 782.5 | 0.019489 |
| 300 | 30 | 90 | 900 | 0.033333 |
| 350 | 49 | 86 | 1003.333 | 0.048837 |
| 400 | 78 | 80.5 | 1073.333 | 0.072671 |

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**Table 2.** Langmuir isotherm data for removal of BY13 and BR46 by NOAC from binary solutions (Sample volume 100 mL, pH=9, *m*=30 mg, *t*=8 min, *T*=25 ºC).

|  |  |  |  |
| --- | --- | --- | --- |
| System | Dye | *C0* /mg L-1  | Langmuir |
| *Ce* /mg L-1 | *R/**%* | *qe/*mg g-1 | *Ce/qe* |
| Binary(1) | BY | 150 | 0.48 | 99.7 | 498.4 | 0.000963 |
| 200 | 10 | 95 | 633.3333 | 0.015789 |
| 250 | 25 | 90 | 750 | 0.033333 |
| 300 | 46 | 84.7 | 846.6667 | 0.054331 |
| 350 | 85 | 75.7 | 883.3333 | 0.096226 |
| Binary(1) | BR | 150 | 2.1 | 98.6 | 493 | 0.00426 |
| 200 | 15 | 92.5 | 616.6667 | 0.024324 |
| 250 | 39 | 84.4 | 703.3333 | 0.05545 |
| 300 | 73 | 75.7 | 756.6667 | 0.096476 |
| 350 | 120 | 65.7 | 766.6667 | 0.156522 |

**Table 3.** Pseudo-second order kinetic model data for removal of BY13 and BR46 by NOAC from binary solutions (100 mL of 150 mg L-1 dyes solution, pH=9, *m*=30 mg, *t*= 2-6 min, *T*=25 ºC).

|  |  |
| --- | --- |
| t/min | Pseudo-second order kinetic model |
| *Dye*  | *Ce* /mg L-1 | *R/**%* | *qt/*mg g-1 | *t/qt* | *Dye* | *Ce* /mg L-1 | *R/**%* | *qt/*mg g-1 | *t/qt* |
| 2 | BY | 58.2 | 61.21 | 306.05 | 0.00653488 | BR | 69 | 54 | 270 | 0.007407407 |
| 3 | 45.3 | 69.8 | 349 | 0.008595989 | 55.5 | 63 | 315 | 0.00952381 |
| 4 | 38.1 | 74.6 | 373 | 0.010723861 | 46.5 | 69 | 345 | 0.011594203 |
| 5 | 28.9 | 80.67 | 403.35 | 0.012396182 | 40.2 | 73.2 | 366 | 0.013661202 |
| 6 | 19.95 | 86.71 | 433.55 | 0.013839234 | 28.73 | 80.85 | 404.25 | 0.014842301 |

**12)** pHpzc: the dependence in Fig.S-2 is peculiar. It is unclear why the authors
did not follow the presentation suggested in cited Ref. 17 (and Refs. cited
therein: J. Haz. Mater. 149 (2007) 269), where pHpzc was taken as the point
at which the curve crossed the line pHﬁnal equals to pHinitial. It is
usually a plateau of similar pHfinals. Authors are demanded to present the
data in the same manner.

With thanks, the necessary revision has been done accordingly (please see Fig. S-2).

**13)** Too many Figs are given. Fig. 1 is not a necessity. It would be ideal for graphical abstract. To be omitted.

With thanks, the necessary change has been done accordingly. Fig. 1 was removed. The number of the figures decreased to 4.

**14)** Line 366, title Section Optimization of NOAC-based ultrasound assisted-adsorption process for simultaneous removal of BR46 and BY13 dyes should be changed, i.e. ultrasound assisted-adsorption deleted, as US is one of the parameters that were optimized below

With thanks, the necessary revision has been done accordingly in the main text.

**15)** Line 371. after adsorption method, add Fig. 5 (a-d).

With thanks, the necessary revision has been done accordingly in the main text.

**16)** Fig. 5a. It is a pity that comparison between removal by pristine AC and
NOAC is given only for pH!

With thanks, the main aim of this work was to study the ability of NOAC on the removal of binary dye solution. In Figure 3a, we just want to show the strong effect of nitrogen functionalization of AC on the removal of both dyes compared to the pristine AC. Therefore, it seems to be not essential to present this comparison for the other parameters as the adsorption ability of AC in binary dye solution was low in comparison with NOAC.

**17)** Legend of Fig. 5a should indicate that AC was also used (besides NOAC), modify accordingly.
With thanks, the necessary revision has been done accordingly (Please see the legend of Fig. 3).

**18)** Lines 381 and 384. It is erroneous to say: for low pH values (pHp<Hzpzc) or for high pH values (pH>pHpzc). Instead, it should be for pH<pHpzc and ….at pH>pHpzc.

With thanks, the necessary revision has been done accordingly in the main text.

**19)** Line 423 Section Effect of initial concentration, and related data-Fig. S-3 should be deleted, since adsorption isotherms are required to be presented in the revised Manuscript. No need to duplicate the data.

With thanks, the necessary revision has been done accordingly in the main text. The related text and Figure were removed.

**20)** Adsorption isotherms, kinetics and thermodynamic study should be presented before desorption study.

With thanks, the necessary revision has been done accordingly in the main text.

**21)** Line 516. Title No need to emphasize …Batch adsorption method. Only so if column studies were presented in Table V, please indicate in such case.

With thanks, the necessary revision has been done accordingly in the main text.

**22)** Line 436. Experim. parameters on Desorption/regeneration study should be given in Experimental.

With thanks, the necessary revision has been done accordingly in the main text.

**23)** Line 461: This indicates that the adsorption of dyes onto NOAC is through ion exchange. In acidic medium due to the protonation, the electrostatic interactions between adsorbent surface and cationic dyes become weaker and then the adsorbed dyes leave the adsorption site.
Question: how do the authors conclude that ion exchange is a mechanism of
adsorption?

The FTIR spectrum of the NOAC adsorbent indicates that hydroxyl and amine groups are present in abundance. So, the sorption of BR and BY on the NOAC adsorbent may be due to the electrostatic attraction between these groups and the cationic dye molecules. At pH above 7.9, the amine groups are deprotonated and negatively charged amine ligands bind to the positively charged BY, BR molecules. This confirms that the sorption of BY and BR by adsorbent was an ion exchange mechanism between the negatively charged groups present in adsorbent and the cationic dye molecule. Moreover, we compared it with the pristine AC. As presented in Fig. 3a, in this case due to the low density of active functional groups on the AC, the removal percentages of cationic dyes were low and quantitative removal values (< 60%) were observed in the pH range of 7-10 (pH>pHPZC).

**24)** Fig. 6. Delete experimental details from the legend.

With thanks, the necessary revision has been done accordingly (please see Fig. 4 of revised manuscript)

**25)** Fig. S-1: Consider omitting AC and combining (b) and (c). Also, apart from numbers, designate important bands to confirm modification. As a matter of fact, FT-IR spectra and related text are not necessary, given the Boehm titration and Table II (elemental analysis), and Raman spectra.

With thanks, the necessary revision has been done accordingly (please see Fig S-1). Moreover, the FT-IR details were transferred to the Supplementary Material.

**26)** Table II. printing error-attention.

With thanks, the necessary revision has been done accordingly in the Table II.