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

AISAN KHALIGH 1\*, HASSAN ZAVVAR MOUSAVI1, ALIMORAD RASHIDI2 and HAMID SHIRKHANLOO3

1 *Department of Chemistry, Semnan University, Semnan 35131-1911, Iran.*

*2 Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), West Entrance Blvd., Olympic Village, Tehran 14857-33111, Iran.*

*3 Research Institute of Petroleum Industry (RIPI), West Entrance Blvd., Olympic Village, Tehran 14857-33111, Iran*

\*Corresponding author: A. Khaligh; Tel: +98 23 3366194; Fax: +98 23 3354110.

E-mail address: akhalighv@gmail.com

**Abstract**

Nanoporous activated carbon (AC) was prepared from eucalyptus leaves via chemical activation with KOH, then treated with nitric acid/urea (NOAC) and finally used as a new adsorbent for simultaneous ultrasound-assisted removal of basic red 46 (BR46) and basic yellow 13 (BY13) dyes from binary aqueous solutions. The NOAC nanoadsorbent was characterized with SEM, TEM, Raman, BET, FTIR, CHN, pHpzc and Boehm titration analysis. Both of the AC and NOAC samples had superior BET surface area of 2222 and 1572 m2 g-1 with average micropore volume of 0.81 and 0.50 cm3 g-1, respectively. First order derivative spectrophotometric method was used for analysis of BY13 in binary mixtures. Small amount of the adsorbent (30 mg) was capable to remove high percentage of dyes (>99%) in a very short time (8 min). The adsorption of dyes followed the Langmuir isotherm and the pseudo-second-order kinetics. The adsorption capacities of NOAC for single solutions of BR46 and BY13 were 1111 and 1250 mg g-1 as well as for binary solutions were 769 and 909 mg g-1, respectively. Adsorption thermodynamics were also explored. Exhausted NOAC was regenerated using HCl (2 M) and reused for five adsorption-desorption cycles with high performance.

*Keywords:*low-cost adsorbent; cationic dyes; fast adsorption; isotherm; kinetics; thermodynamic.

**RUNNING TITLE**: DYES REMOVAL USING MODIFIED AC.

**INTRODUCTION**

Industry dyes are becoming ubiquitous sources of environmental pollution, and their existence has severely affected the aquatic organisms and life cycle. One of the most problematic classes of dyes is the basic dyes called as cationic dyes [1](#_ENREF_1). Toxic cationic dyes of basic red 46 (BR46, single azo class) and basic yellow 13 (BY13, azomethine Class) are widely used in acrylic, nylon, silk, leather, and wool dyeing process. These dyes have carcinogenic, mutagenic, and teratogenic properties which may be related to the presence of nitrogen and positive charge on their structures [2](#_ENREF_2).

Dyes are particularly difficult to remove by conventional waste treatment methods since they are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents. Herein, the removal of dyes from water in an economical way remains an important challenge to scientists. Processes such as coagulation/flocculation, membrane filtration, ion exchange and adsorption are also used for treating dye containing wastewater [3](#_ENREF_3). The later method gain major superiority due to its proven efficiency, ease of operation and insensitivity to toxic material without resulting in the formation of harmful substances as well as the availability of a wide range of adsorbents [4](#_ENREF_4).

Adsorption by activated carbon has been widely used for wastewater treatment due to its exceptionally high surface area and micropore volume, well-developed internal microporosity, favorable pore size distribution, and high adsorption efficiency together with availability of low-cost resources such as plant residues. Recently, An enormous range of waste agricultural materials have been used as activated carbon precursors including rice husk, fruit stone, palm shell, almond shell, coconut shell, pistachio-nut shell, sugar cane bagasse, spent tea leaves, and reedy grass, *etc*. [5](#_ENREF_5). In general, raw materials are initially treated to form charcoal. Then, physical or chemical activation of the charcoal results in activated carbons [6](#_ENREF_6).

Recently, much attention has been paid to surface modification of activated carbons [7](#_ENREF_7). The conventional protocols used for the modification are oxidation, nitrogenation, sulfuration and coordinated ligand anchora [7](#_ENREF_7). Introduction of nitrogen functional groups onto the surface of AC and replacing them with existing oxygen groups has become a subject of great interest nowadays [7](#_ENREF_7), [8](#_ENREF_8). In this trend, oxidation pretreatment of the AC can enhance the incorporation of nitrogen into the carbon [9](#_ENREF_9). Nitrogen modification of AC is an effective method increases its basicity, polarity of its surface and hence the specific interaction with polar adsorbates. To incorporation of nitrogen into the carbon structure, carbons are treated with ammonia, urea, dicyanodiamine, N,N-dimethylformamide, melamine or their derivatives temperatures range from 350 to 900 ºC in different periods of time under nitrogen [9](#_ENREF_9), [10](#_ENREF_10). It has been reported that basic nitrogen functional groups such as amine groups (-NH2, -NH) can be introduced by urea treatment of AC at low temperatures range from 350 to 500 ºC. [10](#_ENREF_10). The presence of heterocyclic nitrogen compounds incorporated in the carbon matrix with free pairs of electrons increase the electron donor capacity of the solid. Therefore, nitrogen-containing ACs are effective adsorbents of positively charged pollutants such as heavy metal ions and cationic dyes through the formation of donor–acceptor complexes [9](#_ENREF_9). Nitrogen-modified ACs have successfully been applied in water decontamination treatments for removal of heavy metal ions (Cu(II), Pb(II), Hg(II), and Cd(II)) [7](#_ENREF_7), [11](#_ENREF_11), [12](#_ENREF_12), anions (CN−, ClO4−, AsO43−) [7](#_ENREF_7), [11](#_ENREF_11), organic substances (benzoic acid, phenol, atrazine) [7](#_ENREF_7), [13](#_ENREF_13), and natural organic matter. Herein, their adsorption was generally enhanced on nitrogenated ACs versus virgin ACs.

UV–Vis spectrophotometric method is usually used as a simple, economic, rapid and accurate technique for dye assessments [14](#_ENREF_14). However, the simultaneous analysis of dyes in binary solution by spectrophotometric methods can be very complex due to the overlapping absorption bands of the dyes and spectral interferences. Derivative spectrophotometry is an analytical technique of great utility in order for resolving this limitation. The derivatisation of zero order spectrum can lead to separation of overlapped signals and elimination of background caused by presence  of the other compounds in a sample [2](#_ENREF_2), [15](#_ENREF_15).

In this study, a low-cost nanoporous activated carbon with a large surface area was prepared from eucalyptus leaves through KOH activation, then treated with nitric acid and urea (NOAC) and finally used as a new nanoadsorbent for the simultaneous ultrasound-assisted removal of basic red 46 (BR46) and basic yellow 13 (BY13) dyes from binary solutions. Eucalyptus leaves as a raw material for the production of activated carbon can be considered as one of the best candidate among the agricultural wastes because it is cheap and quite abundant, especially in arid and semiarid areas like Semnan, Iran. First derivative spectrophotometric method was used for analysis of BY13 in binary mixtures. The influence of several parameters such as pH, temperature, initial concentration of dyes, adsorbent dosage and ultrasonication time for the maximum removal of both dyes was investigated using batch adsorption method. Furthermore, the characterization of dye adsorption was described by the kinetics models, adsorption isotherms and thermodynamic parameters.

**EXPERIMENTAL**

*Apparatus and characterization methods*

A double beam UV-Vis spectrophotometer (Shimadzu, model PC 1650-UV, Japan) with two matched 1-cm quartz cells was used for analysis of the studied dyes. The pH measurements were carried out using a digital pH meter (Metrohm, model 744, Herisau, Switzerland). The ultrasonic bath with heating system (Tecno-GAZ SPA Ultra Sonic System) and a centrifuge (Hettich, model EBA 20, Germany) were used in batch adsorption experiments.

The surface morphology of the adsorbent was characterized using a scanning electron microscopy (SEM, Phillips, PW3710, Netherland) and a transmission electron microscopy (TEM, CM30, Philips, Netherland). The textural parameters of the prepared samples including surface area, pore volume, and pore size distribution were determined by nitrogen adsorption–desorption isotherms at 70 K using a Micrometrics ASAP 2010 system (Micrometric Instruments Co, Cleveland, USA). The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method. Total pore volume was obtained from the volume of nitrogen adsorbed at the relative pressure 0.99. Micropore analysis was made by the t-method and mesopore volume was determined from desorption branch of the isotherm by the BJH (Barrett, Joyner and Halenda) method. Pore size distribution was determined as well. Average pore diameter was also given by 4Vtotal/SBET. Prior to analysis the samples were degassed under vacuum at 200 °C for 2 h. Raman spectroscopy was carried out with an Almega Thermo Nicolet and 532 nm Ar-ion laser excitation source in order to investigate the structural properties and bonding in the virgin and modified ACs. The elemental composition of the samples was measured using the CHN elemental analyzer (Euro Vector S.P.A, model EA 3000, Italy). Oxygen content was calculated as a difference between 100% and the sum of C+H+N. The Fourier transform infrared (FT-IR) spectra were recorded in the range from 4000 to 400 cm−1 using a Bruker IFS 88 spectrometer (Bruker Optik GmbH, Ettlingen, Germany) with KBr pelleting method. The surface acidic and basic groups of the prepared samples were estimated using Boehm titration method. 0.5 g of activated carbon samples were added in test tubes containing 25 mL of NaOH, Na2CO3, NaHCO3, or HCl (0.05 M). The test tubes were shaken for 24 h at 25 ºC and filtrated. Then, 5 mL of the filtrate was pipetted and the excess of base or acid was titrated with HCl or NaOH (0.1 M) solution. The Metrohm pH-meter was employed to monitor the titration. The numbers of acidic sites and basic sites were calculated using titration result [16](#_ENREF_16). The pHPZC (point of zero charge) of the sorbents was determined using the known method as was detailed before [17](#_ENREF_17).

*Chemical reagents and solutions*

All chemicals, with analytical grade purity available, were purchased from Merck (Darmstadt, Germany). Basic Red 46 (BR46) and Basic Yellow 13 (BY13), as model dyes, were used without further purification. The chemical structure and properties of the dyes are shown in Table S-I of Supplementary Material. Deionized water (DI-water) from a Millipore Continental Water System (Bedford, MA, USA) was used for preparation of aqueous solutions. The stock solution of each dye (1000 mg L-1) was prepared by dissolving 250 mg of the dye in 250 mL of DI-water. The experimental and working standard solutions were prepared daily by dilution of the stock solutions.

*Preparation of nanoporous activated carbon*

Eucalyptus leaves (EL) as a raw material for the preparation of AC was obtained from Semnan city, north central Iran. The collected EL was washed with distilled water to remove all the dirt particles, then dried at room temperature for 24 h, and finally ground to powder in a laboratory blender to attain particle size of 0.4-0.8 mm. EL-based activated carbon was prepared via two steps; carbonization of the dried precursor under an inert atmosphere followed by chemical activation of the char impregnated with potassium hydroxide. KOH was used as the chemical activating agent as it is one of the most effective compounds for the production of activated carbons. Details are as follows: the resulting EL powder was first carbonized at 600 ºC for 1 h under N2 flow (200 mL min-1) in a stainless steel tube furnace (1500×50 mm) at a heating rate of 5 ºC min-1 up to 600 ºC. The prepared EL-char was then cooled to room temperature under N2 flow and removed from the reactor.

Nanoporous activated carbon was prepared by mixing the EL-char with KOH solution (KOH: char weight ratio of 2.5:1) at room temperature for 1 h. The slurry was dried overnight at 120 ºC. Then, the impregnated sample was pyrolyzed in the stainless steel tube furnace under N2 flow (200 mL min-1) at activation temperature of 850 ºC, holding time of 1 h and heating rate of 5 ºC min-1. After the activation process, the obtained AC was cooled down to room temperature under N2 flow. Then, in order to obtain pure AC and remove any residual organic and mineral matter, the product was mixed with HCl solution (50% v/v) for 2 h and then washed with hot and cold deionized water until pH of 6–7 was attained. Finally, EL- based nanoporous AC was oven dried at 100 ºC.

*Nitrogen* *modification of nanoporous activated carbon*

The AC surface was first treated with HNO3 solution. 3 g of nanoporous AC was immersed into a flask containing 100 mL of aqueous HNO3 solution (50% v/v) and stirred under reflux at 60 ºC for 3 h. The oxidized AC (OAC) was then cooled to room temperature, washed repeatedly with DI-water until the filtrate was neutral and finally dried overnight at 70 ºC.

In order to prepare the nitrogen-modified nonporous AC (NOAC), urea was used as a nitrogen-rich precursor. 1 g of OAC was impregnated with 10 ml of urea solution (1 M) at room temperature for 2 h. The mixture was oven dried at 80 ºC. Then, the dried sample was annealed by using stainless steel tube furnace at 450 ºC for 1 h in the N2 atmosphere (200 mL min-1) at a heating rate of 5 ºC min-1 up to 450 ºC. The obtained product was cooled down to room temperature under N2 flow, washed with boiling DI-water to remove unreacted urea and finally oven dried at 60 ºC for 6 h.

*Ultrasound-assisted adsorption procedure*

Ultrasound-assistedadsorption experiments were conducted using batch method to elucidate the effect of various parameters such as solution pH, ultrasonication time, adsorbent dose, temperature and initial dye concentration on the removal of dyes from binary solutions.

The necessary amount of NOAC was added to a 250 mL Erlenmeyer flask containing 100 mL of binary dye solution with the initial concentration of 150 mg L-1 (from each of BR46 and BY13) at desired pH value. The solution pH was adjusted by adding negligible volumes of NaOH or HCl diluted solutions. The flask was immersed in an ultrasonic bath (40 kHz, 130 W) at 25 ºC. An aliquot of the sample solution was withdrawn at the pre-determined time intervals and centrifuged at 3000×g for 1 min. Finally the solution was analyzed for the final concentration of dyes by using the UV-Vis spectrophotometer. The removal percentage (R%) and the solid phase dye concentration, *qe* (mg/g) was calculated as:

 (1)

 (2)

Where *C0* and *Ce* are the initial and final dye concentrations in solution phase (mg L-1), respectively; *V* is the volume of the sample solution (L); and *m* is the weight of adsorbent used (g). All the experimental data were the averages of triplicate determinations.

*Adsorption isotherm*

For single and binary dye solutions, the isotherm studies were carried out at different dye concentrations (Table S-II), pH 9 and 25 ºC with 30 mg NOAC and 8 min ultrasonication time according to the above adsorption procedure.

*Adsorption kinetics*

Kinetics of dyes adsorption from binary solutions by NOAC were also investigated according to the adsorption procedure using different ultrasonication times (2-8 min) at optimum amounts of pH, adsorbent dosage and temperature obtained from batch optimization procedure, i.e., 9, 30 mg and 25 ºC, respectively.

*Adsorption thermodynamics*

Thermodynamic studies at different temperatures (15-55 ºC) were carried out by adding 20 mg of NOAC into 100 mL of binary dye solutions (150 mg L-1). The solution pH and ultrasonication time were adjusted in 9 and 8 min, respectively.

*Desorption studies*

Initially, batch adsorption tests were carried out on the fresh NOAC with 100 mL of 150 mg L-1 binary dyes solution at pH 9 containing 30 mg of NOAC. After mixing for 8 min with ultrasonic bath (40 kHz, 130 W, 25 ºC), the mixtures were centrifuged (1 min, 3000×g) and the residual concentrations of dyes in the supernatant solutions were similarly analyzed using UV-Vis spectrophotometer.

The spent NOAC separated from the solution was washed with DI-water to remove the unabsorbed dyes and then oven dried at 70 ºC for 3 h. To choose the effective solvent for desorption of the retained dyes on NOAC, 30 mg of the loaded adsorbent was separately added into 100 mL of various acid-base solutions (HCl, NaOH, H2SO4, CH3COOH) with different concentrations (1-3 mol L-1). The resulting mixtures were agitated for the same time duration as the adsorption tests (i.e. 8 min) in the ultrasonic bath (40 kHz, 130 W, 25 ºC). After desorption, the concentrations of BY13 and BR46 desorbed, Cde (mg L-1), were similarly determined using UV-Vis spectrophotometer. Desorption percent was calculated by:

 (3)

**RESULTS AND DISCUSSION**

*Characterization of adsorbent*

TEM image (Fig. 1(a)) of NOAC shows the porous structure of this sample with pore sizes less than 50 nm. Moreover, as can be seen in this Fig., the carbon layers shift to the graphene sheet as indicated by the arrow. This structure causes an increase in the surface area and the pore volume of the nanoadsorbent. The SEM image (Fig. 1(b)) also confirmed the porous morphology of the sorbent. The activation stage produced extensive external surfaces with quite irregular cavities and pores.

The nitrogen adsorption isotherms for the pristine and nitrogen-modified nanoporous AC samples were displayed in Fig. 1(c). The corresponding isotherm curves of both samples exhibit isotherms of Type I, which is the characteristic of microporous materials. The BJH pore size distribution curves (Fig. 1(d)) for both samples confirm the presence of microporosity and also small mesopores in the range of 2-5 nm. The textural properties of AC and NOAC were presented in Table I. The results show that EL-based nanoporous AC have the extremely high BETsurface area of 2222 m2 g-1 and significant micropore volume of 0.83 cm3 g-1. The obtained BET surface area is attributed to the decline of O2, H2, and N2 contents of the precursor during successive activation steps, creating a nanoporous carbon adsorbent with high porosity and surface area. After modification the surface area decreased to 1572 m2 g-1 with decrease of micropore volume. This is due to the oxidation-nitrogenation reactions which produced functional groups on the surface of AC.

TABLE I.Textural properties of pristine and nitrogen-modified AC.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Sample | BET  suface area,  m2 g-1 | Total pore  volume,  cm3 g-1 | Micropore  volume,  cm3 g-1 | Mesopore  volume,  cm3 g-1 | Average pore diameter\*,  nm | Average particle size,  nm |
| AC | 863 | 2.67 | 52.2 | 0.42 | 0.84 | 5.59 |
| NOAC | 626 | 2.62 | 42.2 | 0.27 | 0.41 | 5.59 |
| \* 4*Vtotal*/*SBET* | | | | | | |

Figs. 1 (e) and (f) show Raman spectra of AC and NOAC. As can be seen in Fig. 2(e), virgin AC shows two broad peaks at about 1345 cm-1 and 1594 cm−1, assigned to D-band and G-band, respectively. For NOAC (Fig. 1(f)), D and G bands were slightly up-shifted to 1350 cm-1 and 1596 cm-1, respectively, which may be related to the changes in hydrogen content of AC sample. The ID/IG ratio (the intensity ratio of the D and G bands) for AC and NOAC was found to be 1.46 and 1.43, respectively, which confirms the presence of defective and amorphous carbon structures in the both samples. Moreover, a shoulder appears at around 1110-1140 cm-1 is attributed to the presence of some sp2-hybridized structures in both samples.

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Fig. 1. (a) TEM image of NOAC, (b) SEM image of NOAC, (C) Nitrogen adsorption isotherms of AC and NOAC, (d) BJH pore size distribution of AC and NOAC, (e) Raman spectrum of AC, and (f) Raman spectrum of NOAC.

C, H, N, O contents of the pristine and modified AC samples were presented in Table II. From the results, compared with the pristine AC, OAC had higher O content originating from oxidation reaction. Also, it is obvious that urea treatment of the OAC led in an incorporation of a significant amount of nitrogen instead of surface oxygen groups and therefore NOAC has low O content compared with OAC.

Oxidation and nitrogenation of AC were further confirmed using Boehm titration method. As can be seen in Table III, oxidation of AC increased total acidity, especially the value of carboxylic acid groups. Modification of OAC with urea resulted in the replacement of surface oxygen groups with nitrogen functional groups such as amine groups, so basicity increased and total acidity decreased. FT-IR spectra of modified AC samples were also recorded. Details about FT-IR spectra were presented in Supplemental Material and Figs. S-1(a)-(b).

For determination of pHPZC of the synthesized samples, the final pH values were plotted versus their corresponding initial pH values (Fig. S-2). The pHPZC was taken as the point at which the curve crossed the line; pHfinal equals to pHinitial. From the results, pHPZC of AC, OAC and NOAC were 6.3, 5.5 and 7.9, respectively. It is obvious that the pHPZC of NOAC is higher than 7 (in the basic range) due to having nitrogen functional groups that are naturally basic; while AC and OAC were acidic due to the acidic oxygen functionalities.

TABLE II.Elemental analysis of pristine and modified AC samples.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Elemental analysis, wt. % | | | | Sample |
| O\* | N | H | C |
| 11.57 | 0.62 | 2.74 | 85.07 | AC |
| 23.15 | 0.85 | 1.78 | 74.22 | OAC |
| 15.15 | 5.98 | 1.85 | 77.02 | NOAC |
| \* O%=100- (C+N+H) | | | | |

TABLE III. Functional groups of pristine and modified AC samples determined by Boehm titration method.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Sample | Surface functional groups, mmol g-1 | | | | |
| Phenolic | Lactonic | Carboxylic | Total acidic | Basic |
| AC | 0.210 | 0.096 | 0.184 | 0.480 | 0.425 |
| OAC | 0.510 | 0.643 | 1.024 | 2.177 | 0.231 |
| NOAC | 0.129 | 0.105 | 0.124 | 0.357 | 1.826 |

*The analysis of the single solutions and simultaneous analysis of the binary solutions*

After preparation of the single solutions of BY13 and BR46 with concentration of 10 mg L-1, the zero order absorption spectra of these solutions were recorded between 200 and 800 nm (Fig. 2(a)). The maximum absorbance of BR46 and BY13 dyes in their single solutions were obtained at 530 nm and 411 nm, respectively. As shown in Fig. 2(a), the absorption spectrum of BY13 dye in binary solution overlapped. Hence, it was not possible to estimate the amount of BY13 dye by direct absorbance measurement in binary solutions. This problem was solved using derivative spectrophotometric method. The first-order derivative spectrophotometry (Fig. 2b) 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. Therefore, First and zero order derivative spectrophotometric methods were utilized for analysis of BY13 and BR46 in binary solutions at 385 nm (1D385) and 530 nm (0D530), respectively, and then calibration curves were made in the concentration range of 2-20 mg L-1 of binary dyes solution. The calibration equations and regression coefficients for BR46 and BY13 dyes in binary solution were obtained as the following:

1D385 (absorbance) = 0.0015 CBY13 + 0.0573, R2= 0.9995

0D530 (absorbance) = 0.0681 CBR46 + 0.0020, R2= 0.9990

Where D is the absorbance value of the studied dye.

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Fig. 2. Spectra of BY13 and BR46 in single and binary solutions (a) zero order spectra, (b) First order derivative spectra (initial dye concentration of 10 mg L-1).

In order to evaluate the accuracy of the zero and first order derivative methods for determining of the BR46 and BY13 concentrations in binary solutions, the recovery studies were done. For this, the binary dye solutions with different concentrations of both components were prepared; then absorbance spectra of these solutions were taken and differentiated (Fig. S-3). The calibration curve of each dye was made and the concentration of the BR46 and BY13 dyes was easily determined (see Table S-III). The recoveries (%) and errors (%) between the measured (Cm) and theoretical (Ct) concentrations were calculated using Eqs. (4) and (5), respectively:

 (4)

 (5)

From Table S-III, high and reasonable recoveries (95-103%) and low error values (<5%) show the efficiency of this method for accurate analysis of both dye concentrations in binary solutions.

*Optimization of NOAC-based adsorption process for simultaneous removal of BR46 and BY13 dyes*

In order to obtain the maximum removal percentages of both dyes, effects of different parameters such as pH, adsorbent dose, sonication time, initial dye concentration and temperature on the simultaneous dye removal were studied and optimized using batch adsorption method (Figs. 3 a-d).

*Effect of the solution pH*

The influence of solution pH on the simultaneous removal of BY13 and BR46 dyes from binary solution by pristine and nitrogen modified AC samples was separately studied over the pH range of 2-10 in conditions of 150 mg L-1 of binary dyes solution, 30 mg adsorbent, 6 min ultrasonication time and 25 ºC, according to the general adsorption procedure. As depicted in Fig. 3(a), by using NOAC adsorbent (pHPZC=7.9) the removal percentages of both dyes were improved with increase in solution pH from 2 to 9 and then constant to 10. Consequently, pH 9 was chosen as optimum for all further studies.

Electrostatic interactions greatly control the adsorption of ionic compounds. For pH<pHPZC, since the surface charge of the adsorbent is positive (because of the protonation of nitrogen and oxygen-containing groups), the electrostatic repulsion between the cationic dye molecules and positively charged adsorbent surface decreases the adsorption of both dyes. For pH>pHPZC, the surface of the adsorbent is charged negatively (due to the deprotonation reaction) and the adsorption of dyes increases due to the electrostatic attraction between the negatively charged adsorbent surface and cationic dye molecules.

As shown in Fig. 3(a), by using pristine AC (pHPZC=6.3) similar observations were also obtained, whereas, the removal percentages of cationic dyes were low and quantitative removal values (< 60%) were observed in the pH range of 7-10 (pH>pHPZC). This is due to the lower density of oxygen-containing groups on AC, which deprotonated at this pH range. So, it can be concluded that physisorption is the main mechanism for dye adsorption by pristine AC.

*Effect of ultrasonic-assisted adsorption time*

Ultrasound irradiation is well known to accelerate chemical process due to the phenomenon of acoustic cavitation. Recently ultrasonic assisted adsorption process has been developed to favor the kinetic of the mass-transfer process of the adsorbate to the adsorbent and to reduce the time required for adsorption [18](#_ENREF_18). In this study, different ultrasonication times from 2 to 12 min were investigated with 100 mL of 150 mg L-1 binary dyes solution (pH=9) containing 30 mg of NOAC at 25 ºC. Fig. 3(b) indicates that with the increase in time, the adsorption rate of the both BR46 and BY13 dyes over the adsorbent increased and the adsorption process reaches equilibrium in only 8 min and then remained constant up to 12 min. From the results, 8 min ultrasonication time was required to bring complete saturation of the active sites of adsorbent, which is excellent for the synthesized NOAC; this was therefore selected as optimum ultrasonication time for further experiments.

*Effect of adsorbent amount*

To optimize the adsorbent dosage for the removal of BY13 and BR46 from aqueous solutions, the adsorption experiments were performed using different adsorbent amounts (5-35 mg) at the optimum pH and contact time, according to the general procedure. As shown in Fig. 3(c), the removal percentage of cationic dyes increased from 45.3% to 98.5% for BR46 and from 56.1% to 99.6% for BY13 with increasing of the adsorbent dose from 5 to 30 mg. This result is due to the increase in adsorbent surface area and availability of more adsorption sites stemming from the increased dose. However, no significant changes in removal efficiency were observed for higher adsorbent doses (>30 mg) due to the fact that the dyes concentration on the surface of the adsorbent and in the solution came to equilibrium with each other. Accordingly, 30 mg of NOAC was used in all subsequent experiments.

*Effect of temperature*

The batch adsorption of BY13 and BR46 were carried out at five different temperatures in the range of 288-328 K with 100 mL of 150 mg L-1 binary dyes solution and 20 mg of NOAC at pH 9, and ultrasonication time of 8 min. As can be seen in Fig. 3(d), the removal efficiencies of both dyes by NOAC increase with the rise in solution temperature from 288 K to 328 K; suggesting that the adsorption process is endothermic. This increase may indicate the increased tendency of cationic dyes due to an increase in kinetic energy with increasing temperature, and this situation leads to more adsorption onto NOAC.

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Fig. 3. Effect of different parameters on the adsorption of BY13 and BR46 dyes onto NOAC:   
(a) Solution pH for both the AC and NOAC adsorbents, (b) Ultrasonication time, (c) Adsorbent dosage, and (d) Temperature, [Conditions: 100 mL of 150 mg L-1 dyes solution, (a) *t*= 6 min, *m*=30 mg, *T*=25 ºC; (b) pH=9, *m*=30 mg, *T*=25 ºC; (c) pH=9, *t*= 8 min, *T*=25 ºC; (d) pH=9, *m*=30 mg, *t*=8 min].

*Adsorption isotherms*

The equilibrium isotherm plays an important role in predictive modeling for analysis and design of adsorption systems. In this study, dye removal process was analyzed using the well-known Langmuir, Freundlich and Tempkin models according to the procedure given in Experimental Section with various initial dye concentrations and constant values of the other parameters for both the single and binary solutions.

A Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, using uniform strategies of adsorption with no transmigration of the adsorbate in the plane of the surface. The Freundlich equilibrium isotherm is used for the description of multilayer adsorption with interaction between the adsorbed molecules. The Tempkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to some indirect adsorbate/adsorbate interactions. The linear forms of the isotherm models are given as [19](#_ENREF_19):

 (6)

 (7)

 (8)

Where *Ce* is the equilibrium concentration of the dye, *qe* is the amount of dye adsorbed per unit mass of adsorbent at equilibrium (mg g-1), *qmax*is the theoretical maximum adsorption capacity (mg g-1), *KL* is the Langmuir constant (L mg-1), *KF* (mg1−(1/n) L1/n g−1) and *n* as the Freundlich adsorption constants are indicators of adsorption capacity and adsorption intensity, respectively, *KT*is the equilibrium binding constant (L mg-1) and *BT* is the variation of adsorption energy (kJ mol-1). Moreover, the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless separation parameter, *RL*, which is defined by equation (9). The values of *RL* between 0 and 1 indicate favorable adsorption process.

 (9)

Isotherm constants calculated from the linear forms of the Langmuir, Freundlich and Tempkin isotherms along with regression coefficient values (*R2*) for three experimental conditions were listed in Table IV. The comparison of the correlation coefficients (*R2*) of the linear isotherm plots indicated that for adsorption of dyes onto NOAC in the single and binary solutions, the Langmuir isotherm yielded a much better fit than the other models at all dye concentrations (Fig. S-4). It was observed that the equilibrium uptake amounts of BY13 and BR46 dyes in binary mixture onto NOAC decreased considerably with increasing the concentration of the other dye resulting in their antagonistic effect. As can be seen from Table S-IV, the values of *RL* were in the range of 0–1, confirming the favorable uptake of both dyes onto NOAC. Therefore, uptake of cationic dyes by NOAC in single and binary systems preferably followed the monolayer adsorption process.

TABLE IV. Isotherm parameter values for removal of BY13 and BR46 by NOAC from single and binary solutions (Sample volume 100 mL, pH=9, *m*=30 mg, *t*=8 min, *T*=25 ºC).

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| System | Dye | *C0* /  mg L-1 | Langmuir | | | Freundlich | | | Temkin | | |
| *qmax* /  mg g-1 | *KL* /  L mg-1 | *R2* | *KF* | *n* | *R2* | *KT* /  L mg-1 | *BT* /  KJ mol-1 | R2 |
| Single | BY | 200-400 | 1250 | 0.186 | 0.993 | 528.48 | 5.72 | 0.985 | 21.33 | 149.97 | 0.962 |
| BR | 200-400 | 1111 | 0.188 | 0.995 | 519.47 | 6.90 | 0.985 | 26.05 | 138.05 | 0.966 |
| Binary  (1)a | BY | 150-350 | 909 | 0.324 | 0.997 | 523.22 | 8.83 | 0.961 | 177.24 | 751.24 | 0.929 |
| BR | 150-350 | 769 | 0.342 | 0.999 | 454.86 | 8.74 | 0.990 | 466.85 | 71.10 | 0.989 |
| Binary  (2)b | BY | 150-350 | 833.3 | 0.265 | 0.993 | 509.28 | 8.63 | 0.978 | 757.48 | 75.98 | 0.967 |
| BR | 150-350 | 555.6 | 0.414 | 0.999 | 511.68 | 22.03 | 0.431 | 107×47.1 | 25.31 | 0.403 |
| a Binary system with constantconcentration of the other dye :150 mg L-1.  b Binary system with variable concentrations of the other dye: 150-350 mg L-1. | | | | | | | | | | | |

*Comparison of the developed NOAC-based adsorption method with others*

A comparison of the maximum adsorption capacity and main adsorption factors of the developed NOAC-based batch adsorption method with other published adsorption methods for removal of BR46 and BY13 dyes from single and binary systems [2](#_ENREF_2), [14](#_ENREF_14), [20-25](#_ENREF_20) were reported in Table V. Obviously, the adsorption capacity of NOAC used in this study is significant high for single and binary systems. This may be attributed to the acid-base character of the carbon surface, its high surface area, micropore volume and pore size distribution. Furthermore, the type and concentration of active sites of adsorbents are responsible for the variation in maximum adsorption capacities between the adsorbents. As can be further seen from Table 5, the considerably short contact time (8 min) along with economic consumption of small amount of adsorbent (30 mg) for the developed NOAC-based adsorption process is a big improvement for the dye removal from single and binary solutions. Therefore, NOAC can be considered to be excellent and potential adsorbent for removal of BR46 and BY13 from single and binary solutions.

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Dyes | Adsorbent | System |  | Optimized conditions | | |  | *qmax /* mg g-1 | | Ref. |
|  | Dye  Concentration,  mg L-1 | Adsorbent dose,  g L-1 | Contact time,  min |  | BY13 | BR46 |
| BR46, BY28 | Bentonite | Sa  Bb |  | 100-400 | 1.00 | 120 |  | ----- | S: 333  B: 208 | [2](#_ENREF_2) |
| BB41, BR18 and BR46 | Graphene oxide | S  B |  | 50 | 0.16 | 60 |  | ----- | S: 476  B: 625 | [14](#_ENREF_14) |
| BR46 | Cerbera odollam AC | S |  | 60 | 0.20 | 120 |  | ----- | 456 | [20](#_ENREF_20) |
| BR46 | nickel oxide NPs- diatomite | S |  | 25-55 | 0.05 | 60 |  | ----- | 124.35 | [21](#_ENREF_21) |
| BR 46, BY28 | Boron industry waste | S |  | 50-300 | 2.00 | 60 |  | ----- | 74.73 | [22](#_ENREF_22) |
| BY13 | Wheat bran | S |  | 50-1000 | 4.00 | 30 |  | 69.06 | ----- | [23](#_ENREF_23) |
| BY13 | Apricot stone AC | S |  | 50-1000 | 6.00 | 35 |  | 134.59 | ----- | [24](#_ENREF_24) |
| BY13 | Sepiolite | S |  | 25-500 | 0.50 | 180 |  | 62.5 | ----- | [25](#_ENREF_25) |
| BR 46, BY13 | NOAC | S |  | 200-400 | 0.30 | 8 |  | 1111 | 1250 | This study |
| B |  | 150-350 | 0.30 | 8 |  | 769 | 909 |
| a Single, b Binary. | | | | | | | | | | |

TABLE V.Comparison of the optimized conditions and maximum adsorption capacity of the NOAC-based adsorption method with other reported methods for removal of BR46 and BY13 from single and binary solutions.

*Adsorption kinetics*

Adsorption kinetics is used to investigate the mechanism and the rate controlling steps of the adsorption process. Characteristic constants of adsorption kinetics were determined using pseudo-ﬁrst-order, pseudo-second-order and intraparticle diffusion models at various ultrasonication times (2-6 min) and optimized values of the other parameters, according to the procedure described in Experimental Section. Linear forms of the studied kinetic models are represented as follows [1](#_ENREF_1):

 (10)

 (11)

 (12)

Where *q1*, *q2* and*qt* are the amount of dye adsorbed at equilibrium and time *t* (mg g-1), respectively, *k1*(min-1) is the equilibrium rate constant of pseudo-first order kinetics and *k2*(g mg-1 min-1) is the equilibrium rate constant of the pseudo-second-order. Moreover, *ki* (mg g-1 min-1/2) and *Ci* are the intra-particle diffusion rate constant and intercept. The calculated parameters and their corresponding *R2* values are presented in Table VI. It can be seen that pseudo-second-order kinetic model provides a good correlation coefficients (*R2*, close to 1) which suggests that the simultaneous adsorption of BY13 and BR46 on NOAC can be better represented by the pseudo-second order model (Fig. S-5). This model is based on the assumption that the rate limiting step may be a chemical sorption involving valence forces through sharing or exchange of electrons between the adsorbent and the adsorbate.

TABLE VI. Kinetic parameter values 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).

|  |  |  |  |
| --- | --- | --- | --- |
| Kinetic model | Constant | Metal ion | |
| BY13 | BR46 |
| Pseudo-first order | *q*1 / mgg-1 | 335.49 | 348.94 |
| *k*1 / min−1 | 0.263 | 0.219 |
| *R*2 | 0.981 | 0.978 |
| Pseudo-second order | *q*2 / mgg-1 | 555.56 | 526.32 |
| *k*2 / g mg-1 min-1 | 10.41× 10-4 | 9.49× 10-4 |
| *R*2 | 0.9935 | 0.9909 |
| Intra-particle diffusion | *C*i | 305.40 | 270.32 |
| *k*i / mg min-1/2 g-1 | 3.755 | 3.874 |
| *R*2 | 0.9561 | 0.9480 |

*Adsorption thermodynamics*

The thermodynamic behaviors for simultaneous adsorption of BY13 and BR46 on NOAC were further investigated in the temperature ranges of 15-55 ºC, according to the procedure given in the Experimental Section. The thermodynamic parameters such as Gibbs free energy change (Δ*G*0), enthalpy (Δ*H*0) and entropy (Δ*S*0) were calculated using the following equations [19](#_ENREF_19):

 (13)

 (14)

Where *R* is the ideal gas constant (8.314 J mol-1 K-1), *T* is the absolute temperature (K), and *Kc* is the thermodynamic equilibrium constant (*qe/Ce*). The values of ∆H0 and ∆S0 were obtained from slope and intercept of van’t Hoff plot, respectively.

The thermodynamic parameters were presented in Table VII. For the adsorption of both dyes onto NOAC, the obtained Δ*H*0 values were positive which indicates the endothermic nature of the adsorption process; which is in good agreement with the results that the adsorption of dyes increased with the increasing temperature. Negative Δ*G*0 values showed the spontaneous nature of adsorption process. Also, the positive values of Δ*S*0 show the increased randomness at the solid/solution interface.

TABLE VII. Thermodynamic parameters 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*= 8 min).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Dye | Parameter | *T* / K | | | | |
| 288 | 298 | 308 | 318 | 328 |
| BY13 | *∆H0*/ kJ mol-1 | 36.51 | 36.51 | 36.51 | 36.51 | 36.51 |
| *∆G0* / kJ mol-1 | -5.513 | -6.825 | -8.125 | -9.640 | -11.418 |
| *∆S0* / kJ mol-1K-1 | 0.146 | 0.146 | 0.146 | 0.146 | 0.146 |
| BR46 | *∆H0*/ kJ mol-1 | 34.57 | 34.57 | 34.57 | 34.57 | 34.57 |
| *∆G0* / kJ mol-1 | -2.499 | -5.133 | -8.329 | -12.365 | -17.334 |
| *∆S0* / kJ mol-1K-1 | 0.136 | 0.136 | 0.136 | 0.136 | 0.136 |

*Desorption and regeneration studies*

An ideal adsorbent should exhibit not only high sorption capacity, but also easy regeneration and stability during several adsorption–desorption cycling, which can significantly reduce the overall cost of the adsorbent. Desorption studies also help to elucidate the nature of adsorption and recycling of the spent adsorbent and the dye [26](#_ENREF_26). First, the best desorption solvent was selected according to the procedure explained in the Experimental Section and then the number of adsorption-desorption cycles using this solvent were investigated.

Figs. S-6 (a) and (b) show the effects of various solvents for desorption of BY13 and BR46 dyes from NOAC, respectively. Among these, HCl (2-3 mol L-1) and H2SO4 (3 mol L-1) solutions provided higher desorption efficiency (R~100%) for both BY13 and BR46. Thus, in order to use low concentration of organic solvent, HCl (2 mol L-1) was specified as the best solvent for quantitative desorption of dyes. 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.

To investigate the long-term stability of NOAC, it was subjected to several adsorptions and desorption cycles under the optimized conditions, as described above. The adsorption process was started with fresh NOAC and after the desorption step using 100 mL of HCl (2 mol L-1), the regenerated adsorbent was reused for the subsequent adsorption-desorption cycle. As shown in Fig. 4, The NOAC nanosorbent can be used for 5 adsorption–desorption cycles without decrease in the removal percentages of BY13 and BR46. At the sixth cycle, the removal percentages of BY13 and BR46 were decreased to 96%, and 94%, respectively. However, after 16 adsorption-desorption cycles, the removal percentages of BY13 and BR46 were decreased to 16% and 45%, respectively.

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Fig. 4. Reusability of the NOAC under the optimized conditions.

**CONCLUSIONS**

In the present paper, eucalyptus leaves-based nanoporous activated carbon was prepared via chemical activation with KOH, oxidized with nitric acid, then modified with urea and finally introduced as a new and efficient adsorbent for simultaneous ultrasound assisted-removalof BR46 and BY13 dyes from binary solutions. The AC and NOAC generated both high specific surface area and high micro pore volume. The first-order derivative spectrophotometric method was successfully applied for determination of BY13 in binary solutions. The optimum conditions of batch adsorption were found to be pH 9, initial BR and BY concentrations of 150 mg L-1, NOAC dosage of 30 mg, sonication time of 8 min, and temperature 25 ºC. The data indicated that the adsorption kinetics of dyes on NOAC followed the pseudo-second order. The equilibrium data were correlated reasonably well by Langmuir adsorption isotherm in both the single and binary mixtures. Based on thermodynamic studies, the adsorption of dyes was both endothermic and spontaneous. The remarkable advantages of the developed NOAC-based adsorption process include its high removal performance (>98.5%) in a very short time and economic consumption of only 30 mg of NOAC adsorbent which has superior adsorption capacities and also can be regenerated and reused for 5 adsorption-desorption cycles. In conclusion, NOAC can be effectively used as an adsorbent for the removal of cationic dyes from single and binary systems.

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