Production of an Efficient Magnetic Adsorbent From Babassu Coconut Endocarp and Ni Particles for Easy Dye Removal From Mimetic Contaminated Effluents

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Abstract

Ni metal particles, with sizes ranging from 70 to 110 nm, dispersed in activated carbon produced from the babassu coconut endocarp (BAC) were successfully synthesized and evaluated by scanning electron microscopy, dispersive energy X-ray spectroscopy, flame atomic absorption spectroscopy and powder X-ray diffraction. These hybrid BACNi-X materials (where X is the Ni / BAC ratio, equal to 10, 20 or 30) exhibit crystalline Ni particles with suitable magnetic properties, shown by increased saturation magnetization and a gradual reduction in coercive fields (varying 80 to 150 Oe) as the Ni content increases. Relatively large values of pore volume (in the range of 0.28-0.37 cm³/g), specific surface area (560-740 m²/g) are achieved, favoring their applications for magnetic remediation of mimetic contaminated effluents. All hybrid samples were tested positively for the adsorption of methylene blue in contaminated synthetic effluents and the greatest removal was achieved by the hybrid sample BACNi-10, which has the largest specific area and reasonable magnetic properties that allowed the manipulation of the sample by an external field.

Introduction

Water pollution is one of the world's biggest concerns due to the accumulation of pollutants that are extremely harmful to health. The pollutants of water bodies have both inorganic and organic origin. Among the inorganic pollutants are heavy metals, liberated mainly by different extractive and industrial parcs. The most dangerous contaminants are lead, mercury, zinc, copper, cadmium, iron, chromium, arsenic, among others (Chowdhury et al. 2016; Li et al. 2002; Li et al. 2005; Mousavian et al. 2017; Mubarak et al. 2013; Ogundele et al. 2017; Ruthiraan et al. 2015). The consequences of potentially toxic elements pollution include, in addition to disrupting food chain, the bioaccumulation of these metals in human and animal tissues that also indirectly causes various problems to human health, including not only high probability of developing cancer and central nervous system atrophy, but also mental retardation, gastrointestinal disorders and several other diseases (Li et al. 2002; Mousavian et al. 2017; Acharya et al. 2009).

Among the organic pollutants are dyes, which are widely used in the textile and cellulose industries and are dumped in considerable quantities into waterbodies. Dyes, such as methylene blue, Congo red and others, make water very toxic for human or animal consumption due to the difficulty of degradation and resistance to anaerobic decomposition, leading to problems, such as: dermatitis and respiratory tract issues (Ardejani et al. 2007). However, the greatest risk is the oral ingestion of these compounds because dyes, if catalyzed by specific enzymes in the body, can generate substances with carcinogenic and/or mutagenic properties (Lellis et al. 2019).

Several techniques have been used for the treatment of effluents, like: biofiltration, flow microfiltration, adsorption, electrocoagulation, slow filtration, flocculation, flotation, membrane separation processes, and advanced oxidative processes (Abdel-Ghani and Elchaghaby 2007; Abidi et al. 2015; Alhaji et al. 2016; Krzeminski et al. 2016; Martins et al. 2017; Mohanty et al. 2005; Mullai et al. 2017). Among them,

the adsorption technique is widely used for the removal of inorganic and organic compounds dissolved in water, which uses low-cost materials, such as: clays, alumina, mesoporous silicas, zeolites and activated carbon as adsorbents (Abidi et al. 2015; Fungaro and Bruno 2009; Tong et al. 2014; Tong et al. 2016).

In water treatments, adsorption on activated carbon is considered one of the most effective techniques, and its advantages include high efficiency in the removal of microcontaminants and ease of operation, in addition to low cost in obtaining the raw material (Al-Degs et al. 2000; Fungaro and Bruno 2009; Tong et al. 2016). Activated carbon can be produced from numerous raw materials with a high carbonaceous content, as: wood, petroleum coke and agricultural residues in general (sugarcane bagasse, straw and corn husks, coffee straw, rice husks and coconut shells) (Coelho et al. 2012). Among these agricultural wastes, we highlight the shells of babassu coconut, which are a byproduct of the exploitation of the babassu palm (*Attalea speciosa* Mart. ex Spreng) (Cavallari and Toledo 2016). This constitutes an important economic activity in many regions of northeastern Brazil, mainly in the use of almonds, due to the great interest in the extraction of oil to produce biodiesel (Da Rós et al. 2014; Lima et al. 2007). Other potentially relevant uses of this agrowaste include the production of charcoal, activated carbons and cellulosic products (Brito et al. 2019; Emmerich and Luengo 1996; Teixeira 2008).

The adsorbents with magnetic properties have highly been targeted due to their possibility of been removed from the effluent treatment medium with the help of a magnet (Thines et al. 2017). In the work of Liu et al. (2013), $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ magnetic nanoparticles were synthesized for the adsorption of the methylene blue dye and the subsequent removal of the adsorbent taking advantage of its magnetic properties. In addition, Ruthiraan et al. (2017) obtained surprising results when using a magnetic adsorbent synthesized from the pyrolysis of mangosteen peel and ferric oxide, which showed removal efficiency above 90% for the adsorption of Cd^{2+} ions and methylene blue dye. However, there was no clear elucidation as to whether the magnetic particles also contribute to the adsorption capacity or only assist in the removal of the adsorbent. In brief, the above works have shown that the transformation of an activated carbon adsorbent into a magnetic adsorbent can be successfully achieved by introducing elements with ferromagnetic characteristics, as cobalt, nickel, and some iron oxides, into the porous structure of the matrix.

In this sense, this work reports the production of activated carbon from the endocarp of babassu coconut, using the method of physical activation for the development of porosity. In addition, the activated carbon was converted into an adsorbent with magnetic properties by adding metallic nickel to its composition. Then, the material's removal capacity was verified by adsorption tests using a methylene blue dye solution, visible in wastewater at low concentration (1 mg L^{-1}) (Ruthiraan et al. 2017). The obtained results illustrate the benefits of combining the large porosity of the carbonaceous matrix and the ferromagnetic behavior of the Ni particles, leading to the production of low-cost and environmentally friendly magnetic adsorbents with high potential for use in water treatment processes.

Experimental Section

Materials

Nickel nitrate hexahydrate $\text{Ni}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 98%, Dinâmica Química Contemporânea®), sodium hydroxide (NaOH, 97%, QM™) and methylene blue (MB) (95%, Sigma-Aldrich®) were commercially available and used without prior purification. Babassu coconut was harvested in Açailândia (MA), Brazil.

Preparation of activated carbon

Activated carbon was prepared from the babassu coconut endocarp, previously separated from the other constituents of the coconut. The endocarp was crushed to obtain a granular material, from which 30.0 g were submitted to the activation process in a tubular furnace, under argon atmosphere and steam, at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$ to $800\text{ }^\circ\text{C}$ for 3 h. The injection of water was started when the temperature reached $300\text{ }^\circ\text{C}$, using a peristaltic pump and a physical activation apparatus previously described in Brito et al. (2019). The activated sample was macerated and sieved through a 70-mesh screen ($210\text{ }\mu\text{m}$ opening size) to homogenize the macroscopic grain size. The activated carbon produced from the endocarp of babassu coconut was named "BAC" and the activation process was repeated twice, producing 9.0 g of activated carbon.

Synthesis of Ni particles supported on BAC: hybrid BACNi-X

Ni particles supported on BAC were successfully synthesized from the BAC precursor and a proportional mass of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to obtain samples containing 10, 20 and 30 wt. % of Ni/BAC ratio, named hybrid BACNi-10, BACNi-20 and BACNi-30, respectively. Firstly, the Ni^{2+} salt was dissolved in 50.0 mL of distilled water and then 2.0 g of BAC were added. This mixture was stirred at 100 rpm at room temperature. After that, an excess of NaOH (0.1 mol L^{-1}) was added until pH 12, at a rate of 0.32 mL min^{-1} . The samples were filtered under vacuum and dried for 24 h at room temperature. Finally, 1.4 g of each sample were heated at $800\text{ }^\circ\text{C}$, at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$, under argon atmosphere, to produce Ni particles supported on the activated carbon matrix.

Characterization of the hybrid BACNi-X samples

A Perkin Elmer AAnalyst 800 flame atomic absorption spectrometer equipped with a deuterium-arc lamp background corrector was used for absorbance measurements at 232.0 nm for nickel. The operating conditions were those recommended by the manufacturer, unless specified otherwise. Replicate numbers in each analysis were equal to three.

Thermogravimetry (TG) curves were recorded on a Shimadzu™ TGA-50H thermal analyzer; the samples were heated from 30 to $1000\text{ }^\circ\text{C}$ at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ under O_2 flow (flow rate of 50 mL min^{-1}).

Textural analysis was carried out by recording N_2 adsorption/desorption isotherms at 77 K using an Autosorb-1 instrument (Quantachrome Instruments™). The specific surface area values were determined

by the Brunauer-Emmet-Teller (BET) method, whereas the micro- and mesopore volumes were obtained using the non-local density functional theory (NLDFT) approach (Lowell et al. 2004).

Surface morphology was studied by scanning electron microscopy (SEM) on a Shimadzu SS-550 microscope operating at 15 kV, equipped with an accessory module for energy dispersive X-ray spectroscopy (EDX) analyses. The magnetic properties were evaluated on a Quantum Designs™ 6000 PPMS (Physical Property Measurement System) equipment, using a mass of 0.60 g; the magnetization (M) as a function of magnetic field (H) curves were recorded at room temperature (300 K) with a maximum sweep H-field of 6.0 kOe.

The powder X-Ray diffraction (PXRD) patterns were recorded on a Shimadzu™ XRD-6000 diffractometer, operating at 40 kV and 30 mA, using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), in the 2θ range from 10 to 80° at a rate of $0.002^\circ \text{ min}^{-1}$. The obtained diffraction patterns were analyzed and compared with the crystallographic structures provided by the Joint Committee on Powder Diffraction Standards (JCPDS), International Centre for Diffraction Data (ICDD), available in PCPDFWIN software version 2.3 (PCPDFWIN 1996). In addition, the obtained X-ray diffractograms were adjusted using the software MAUD (Materials Analysis Using Diffraction) (freeware) (Lutterotti et al. 2010). The fittings of the PXRD patterns were performed to determine the average crystallite sizes and the volume fractions of the crystalline phases present in the analyzed samples.

Adsorption behavior of the hybrid BACNi-X samples

For the adsorption tests of MB by hybrid BACNi-X materials (X = 10, 20 and 30), a three leveled (-1, 0, + 1) full factorial design was performed to evaluate the influence and the interaction of independent variables (Ni content in activated carbon and adsorption time) on the response variable (concentration of the MB solution after adsorption). The values of the independent variables for each level are the following: nominal Ni/BAC ratio (wt. %) 10(-1), 20(0) and 30(+ 1), and adsorption times (min) 15(-1), 45(0) and 60(+ 1). The combination between them and the correspondent experiment denominations are shown in Table 1.

The adsorptions were performed at room temperature by adding, separately, 5 mg of each hybrid BACNi-X sample in 10 mL of a mimetic contaminated effluents composed by 20 ppm MB aqueous solution. After the adsorption times (Table 1), the hybrid BACNi-X samples were removed from the solution and the remaining MB concentration was evaluated on a UV-VIS Lambda 45 PerkinElmer spectrophotometer operating at 664 nm.

The results were analyzed from the Effect Table and the Response Surface Graph generated by the Statistica Software (Stat Soft Inc 2014). In addition to the factorial design results, the adsorption process was carried out in pure activated carbon (BAC-0) with the same adsorption time variation, in order to verify the role played by the presence of the Ni particles on the adsorption process.

Table 1
Experiments performed and the respective combination of the independent variable levels.

	Factor 1	Factor 2
Experimental conditions	Ni/BAC ratio in wt. % (level/x)	Adsorption time in min (level/y)
1 (BAC-10%-15 min)	10(-1)	15(-1)
2 (BAC-20%-15 min)	20(0)	15(-1)
3 (BAC-30%-15 min)	30(+ 1)	15(-1)
4 (BAC-10%-45 min)	10(-1)	45(0)
5 (BAC-20%-45 min)	20(0)	45(0)
6 (BAC-30%-45 min)	30(+ 1)	45(0)
7 (BAC-10%-60 min)	10(-1)	60(+ 1)
8 (BAC-20%-60 min)	20(0)	60(+ 1)
9 (BAC-30%-60 min)	30(+ 1)	60(+ 1)

Results And Discussion

Determination of the Ni content

The Ni content in hybrid BACNi-10, BACNi-20 and BACNi-30 samples were determined by FAAS and the found values are 13, 23 and 27 wt. %, respectively (Table 2). These values are reasonably close to the initial Ni contents (10, 20 and 30 wt. %, respectively). The differences between the actual and the nominal Ni/BAC ratios can be due to the loss of carbonaceous matrix during the heat treatments at 800 °C applied to convert the nickel hydroxide into metallic nickel particles.

Thermal analysis

The thermal behavior of the hybrid BACNi-X samples under oxidizing atmosphere are shown in Fig. 1. The first decomposition step is observed up to 115 °C and corresponds to the release of adsorbed water, with weight losses of 5% for the pure BAC sample and 3% for all hybrid BACNi-X samples. The second decomposition step occurs between 450 and 500 °C, with weight losses of 88, 75, 63 and 59 % to BAC, BACNi-10, BACNi-20 e BACNi-30, respectively. This step corresponds to the oxidation process of the carbonaceous matrix and the reduction of the weight losses (i.e., the fixed carbon contents) with the increase in the Ni contents is obviously associated with the growth of the ash contents. In addition, it is observed a synergism between the Ni/BAC ratios and the thermal stability of each sample, with the oxidation temperature increasing along with the Ni/BAC ratio.

Textural analysis

The adsorption and desorption isotherms of N₂ at 77 K for the pure BAC and hybrid BACNi-10, BACNi-20 and BACNi-30 samples are shown in Fig. 2. These curves are similar to type I isotherms, due to the abrupt increase in the adsorbed amount of N₂ at low relative pressures, which is a feature typical of microporous materials (Lowell et al. 2004; Sing 1985). Also, the specific surface area values and the volumes of micro/mesopores are also shown in Table 2. As expected, the pure BAC sample presents the largest specific surface area, corresponding to 824 m² g⁻¹, while for the hybrid BACNi-X samples, the inclusion of the Ni particles causes a reduction of the specific surface area values, being equal to 741, 608 and 561 m² g⁻¹ for the hybrid BACNi-10, BACNi-20 and BACNi-30 samples, respectively. Therefore, the lower the Ni/BAC ratio, the higher the specific surface area. These results are satisfactory, since other activated carbons obtained by physical activation typically exhibit specific surface area values in the range of 200–1300 m² g⁻¹ (Nabais et al. 2008; Reddy et al. 2013; Rodriguez-Reinoso et al. 1995; Sun and Jiang 2010). The pore volumes of the hybrid BACNi-X samples follow the same trend of the specific surface area as a function of the increase of Ni/BAC ratio. All hybrid samples exhibit micropore volumes accounting for 85–89 % of the total pore volume. It is interesting to note that the mesopore contribution to the total pore volume increases slightly with the increase of the Ni content.

The main reason for the decrease in the specific surface area values and pore volumes as a function of the Ni/BAC ratio is the effective reduction in the mass fraction of the porous carbon matrix (as revealed by the TG results) in the hybrid BACNi-X samples. Moreover, it is possible that some obstruction of the porous structure of the activated carbon also contributes to the porosity reduction in the composite samples. It is also worth pointing out that the increase in the relative fraction of mesopores in the total pore volume of the hybrid BACNi-X samples can be associated with the surface contribution of the Ni-containing particles, similarly to what has been observed in other nanostructured systems (Gonçalves et al. 2015).

Table 2
Ni content and textural properties of the pure BAC and hybrid BACNi-10, BACNi-20, BACNi-30 samples

Samples	Ni content (wt. %)	S _(BET) (m ² g ⁻¹)	V _{micropore} (cm ³ g ⁻¹)	V _{mesopore} (cm ³ g ⁻¹)
BAC	-	824	0.326	0.039
BACNi-10	13	741	0.328	0.046
BACNi-20	23	608	0.258	0.046
BACNi-30	27	561	0.241	0.043

Particles morphology

SEM and TEM images of the hybrid BACNi-10, BACNi-20 and BACNi-30 samples are shown in Fig. 3. It is possible to see submicron spherical particles homogeneously dispersed on the carbonaceous matrix (Zieliński et al. 2007). A selected area of the hybrid BACNi-10 sample, demarcated by a red square in

Fig. 3(a), was submitted to EDX analysis. It shows the distribution of the elements carbon (intense peak) and low signals due to oxygen and Ni atoms. These results clearly indicate the presence of submicron Ni-containing spherical particles on the surface of the hybrid BACNi-X samples.

Structural characterization

The PXRD patterns of all synthesized samples are shown in Fig. 4. The diffractogram of the pure BAC sample exhibits broad peaks at ca. 23° and 43° , assigned to the (002) and (200) reflections of the turbostratic structure of the carbon matrix (Carreño et al. 2002; Li et al. 2007; Silva and Rezende 2018; Zanoteli et al. 2014). A small peak ascribed to silicon dioxide (SiO_2) is also detected at 22.4° , in accordance with Freitas et al. (2000), that assigned this peak around 22° and it is a consequence of the natural occurrence of Si-containing compounds in the endocarp of babassu coconut. Besides, the diffractograms of the hybrid BACNi-10, BACNi-20 and BACNi-30 samples show two intense diffraction peaks at 44.5° and 51.9° and a lower intense peak at 76.5° , which correspond to (111), (200) and (222) reflections, respectively, of the face centered cubic (fcc) structure of the metallic Ni (Zieliński et al. 2007). A remaining phase of nickel oxide (NiO) in the material is present in all hybrid BACNi-X samples, identified by low intensity diffraction peaks at 37.3° , 43.3° and 62.9° , associated with the reflections (111), (200) and (220) of the fcc structure of NiO, respectively (Zieliński et al. 2007). Finally, the presence of Ni and O atoms in the X-ray diffractograms agrees with the EDX map shown in Fig. 3(a).

The PXRD patterns of the hybrid BACNi-X samples were adjusted using the MAUD software (Lutterotti et al. 2010), as illustrated in Fig. 5 for a representative sample. These structure refinements allowed the calculation of the volume fraction of each crystalline phase (Ni and NiO) and the determination of the corresponding average crystallite sizes, which are listed in Table 3. These results show that both the Ni and the NiO average crystallite sizes increase as the Ni/BAC ratio increase. At the same time, the volume fraction of the metallic Ni phase also grows, reaching a value close to 90 % for the hybrid BACNi-30 sample. It is important to note that these crystallite sizes are somewhat smaller than the Ni particle sizes observed in the SEM and TEM images shown in Fig. 3 (albeit they are all the same order of magnitude), thus suggesting a polycrystalline nature for those particles (Gonçalves et al. 2015).

Table 3
Volume fractions and average crystallite sizes of the crystalline phases identified in the PXRD patterns of the hybrid BACNi-X samples

Samples	Phase	Crystalline phase content (%)	t (nm) (± 1 nm)
BACNi-10	Ni	69.7	66
	NiO	30.3	12
BACNi-20	Ni	78.0	69
	NiO	22.0	14
BACNi-30	Ni	89.6	116
	NiO	10.4	18

Magnetic properties

The magnetic properties of the hybrid BACNi-10, BACNi-20 and BACNi-30 samples were investigated by recording the magnetization (M vs. H) curves shown in Fig. 6. These curves clearly reveal the ferromagnetic character of the analyzed materials (magnetic saturation regime and non-zero coercive field). In particular, the hysteresis $M(H)$ cycles present coercive field (H_c) ca. 100 Oe, as observed in the inset of Fig. 7, and informed in Table 4. Thus, it reflects the soft-like ferromagnetic character of the Ni nanoparticles. The values of the saturation magnetization (M_s in emu/g) are also given in the same table. As can be seen, Fig. 6 clearly shows a correlation of M_s with the content of metallic Ni in the samples (estimated from the PXRD results and considering the bulk densities of Ni and NiO). This trend is understandable, since the NiO phase (exhibiting bulk antiferromagnetic behavior at room temperature) is not expected to contribute significantly to the saturation magnetization of the hybrid BACNi-X samples, which is, therefore, chiefly determined by the content of the ferromagnetic phase (metallic Ni) in these materials (Coey 2009).

As for the coercive field, the decrease of H_c as a function of the Ni content can be understood considering that relatively large ferromagnetic particles, as those observed in the SEM images (Fig. 3), preferably form multiple magnetic domains, for which the coercive field is expected to be low (Crangle and Goodman 1971; Leslie-Pelecky and Rieke 1996). On the other hand, when the ferromagnetic particles exhibit sizes below a give critical diameter (around 55 nm for Ni), the formation of magnetic single domains is preferred and the coercive field increases, because changes in the magnetization can no longer occur by modifications in the multi domain structure (e.g., domain walls displacement) and must be accomplished by the rotation of the magnetic moments of the whole single domain particles (Coey 2009). In the case of the hybrid BACNi-X samples, the PXRD results indicate that the average crystallite size of the metallic Ni phase grows with the increase in the Ni content (Table 3), which, in the mentioned scenario, explains the trend of reduction of the H_c values, also considering that these materials are composed of Ni-containing ferromagnetic particles with a broad size distribution (Khan et al. 2020).

Table 4

Total Ni content determined by FAAS and by PXRD, saturation magnetization (M_s) and coercive field (H_c) of the hybrid BACNi-X samples

Samples	Ni content (wt. %)*	Metallic Ni content (wt. %)**	M_s (emu/g)	H_c (Oe)
BACNi-10	13	9.8	3.3	150.0
BACNi-20	23	19.0	6.2	113.1
BACNi-30	27	24.8	12.3	84.4
* Ni contents determined by FAAS.				
** Ni content calculated by PXRD (after considering the densities of the Ni and NiO phases).				

Statistical analysis of the adsorptive capacity of the hybrid BACNi-X samples

The adsorption process results, obtained in the factorial design experiments, are summarized in Table 5. The value of the response variable corresponds to the concentration of the MB solution at the end of the adsorption process conducted for each sample, indicating the adsorption capacity of the hybrid BACNi-X samples.

The adsorption process (Fig. 7) shows a better result for the test performed with a longer adsorption time (60 min), firstly evidencing the importance of this parameter for the efficient removal of the organic dye from a synthetic solution, and secondly improving the adsorption process in the pores of the adsorbent materials. In addition, the sample with the lowest Ni/BAC ratio (BACNi-10) and the highest specific surface area showed the best adsorption result, evidenced by the lower remaining concentration of MB in solution (5.47 ppm). This relatively low amount of Ni in this material is sufficient to allow the removal of the magnetic adsorbent from the MB synthetic solution by magnetic attraction (Calimli et al. 2020; Kim et al. 2018; Tao et al. 2019).

Table 5

Results of the factorial design experiments for the adsorption process of MB by the hybrid BACNi-X samples

Variable Response: Methylene Blue Concentration (ppm)					
Samples	Ni/BAC ratio (wt. %)	Adsorption time (min)			
		15	45	60	
BACNi-10	13	9.23	8.42	5.47	
BACNi-20	23	9.17	9.17	7.80	
BACNi-30	27	9.17	9.17	8.77	

The Effect Table, Table 6, presents the effect of an independent variable and the interaction between independent variables (the factors) in a dependent variable (the response variable), within a 95% confidence limit. The p-value describes the probability of result significance, in which values smaller than 0.05% indicate that a certain factor exerted influence on the response variable. From the interpretation of the statistical model, only the interaction between factors influences considerably the response variable value (p-value = 0.000009); therefore, the combination between Ni concentration and adsorption time presents greater significance in the result (Amorim et al. 2018; Santos and Luz 2020).

The Factor 2 (adsorption time) influences the variable response (concentration of the MB solution after adsorption), so that longer adsorption times leads to lower dye concentrations, thus indicating higher adsorption of MB by the hybrid BACNi-X samples. Oppositely, the Factor 1 influences negatively the response variable, since the increase in Ni/BAC ratio (with the consequent reduction in the specific surface area values and pore volumes) results in a more concentrated solution, which means lower adsorption by the hybrid BACNi-X samples.

Table 6
Effect Table for the adsorption process of MB by the hybrid BACNi-X samples

Factor	Effect	Std.Err.	Coefficient	Std.Err.	p-value
Mean/interactions	8.59	0.30	8.59	0.30	9.0×10^{-6}
Ni/BAC ratio (wt. %) (L)	1.33	0.74	0.67	0.37	1.45×10^{-1}
Ni/BAC ratio (wt. %) (Q)	0.34	0.64	0.17	0.32	6.20×10^{-1}
Adsorption time (min) (L)	-1.84	0.74	-0.92	0.37	6.62×10^{-2}
Adsorption time (min) (Q)	0.96	0.65	0.48	0.32	2.13×10^{-1}

The coefficients of Effect Table were used to construct a mathematical model that describes the interactions between the two factors studied at three levels, and the obtained equation is:

$$z(x,y) = 8.59 + 0.67x + 0.17x^2 - 0.92y + 0.48y^2 \quad (1)$$

where y is the response variable, x_1 corresponds to Ni/BAC ratio (Factor 1) and x_2 is the adsorption time (Factor 2).

The Surface Graph, Fig. 8, shows a three-dimensional relation of the factors and allows a visual analysis of the results, represented by a uniform surface. The independent variables (Factors 1 and 2) are found on the x and y axes, and the response variable on the z axis.

These results then show that it is possible to prepare efficient magnetic adsorbents containing submicron Ni particles dispersed in biomass-derived activated carbons, using a simple impregnation route followed by heat treatments. The use of a relatively low Ni loading (~ 13 wt. %) allows the production of a magnetic adsorbent with sizeable porosity (specific surface area $\sim 740 \text{ m}^2 \text{ g}^{-1}$) that can remove a large amount of methylene blue in aqueous solution. Furthermore, this material exhibits strong ferromagnetic properties at room temperature, which allow the easy separation of the magnetic adsorbent from the aqueous solution after the end of the adsorption process. Finally, it is worth stressing that, although this work is concerned only with the adsorptive properties of the produced hybrids, these materials composed of submicron Ni-containing particles supported on a porous matrix are of potentially high interest for applications in fields such as heterogeneous catalysis and hydrogen storage, among others (Zieliński et al. 2007; Careño et al. 2002; Zanolli et al. 2014; Li et al. 2010; Donald et al. 2010).

Conclusion

The successful synthesis of submicron Ni particles dispersed in biomass-derived activated carbons gave rise to stable and magnetic adsorbents useful for the adsorption of methylene blue from mimetic contaminated effluents and that can be easily separated from the aqueous medium using a magnet. The predominance of metallic Ni particles, evidence by the analysis of X-ray diffraction results, is responsible for the magnetic behavior of the adsorbents, even at the lowest Ni loading (~ 13 wt. %). The presence of the Ni particles reduces the specific values of pore volume and surface area of the prepared samples due to the reduction of the fraction of the material effectively associated with the porous carbon matrix. By a (2^3) factorial design for the adsorption of methylene blue by the hybrid BACNi-X samples, a satisfactory adsorption and magnetic separation are obtained for the hybrid BACNi-10 sample at 60 min of contact with the dye synthetic solution, evidencing the benefits of combining the large porosity and the ferromagnetic behavior of the produced adsorbents. These results show then that it is possible to prepare efficient Ni-containing magnetic adsorbents using activated carbons derived from a lignocellulosic waste material and following a simple impregnation route followed by heat treatments. A small amount of Ni is sufficient to carry out the magnetic separation process while preserving the porous structure of the material and thus ensuring a good adsorption efficiency.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Availability of data and materials

All data generated or analysed during this study are included in this published article.

Competing interests

The authors declare that they have no competing interests.

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Figures

Figure 1

TG curves of the hybrid BACNi-10, BACNi-20 e BACNi-30 samples, under oxidizing atmosphere

Figure 2

N₂ adsorption/desorption isotherms of the pure BAC and hybrid BACNi-10, BACNi-20, BACNi-30 samples

Figure 3

SEM images of the hybrid (a) BACNi-10 (EDX spectrum in the inset), (b) BACNi-20 and (c) BACNi 30 samples, and TEM images of the hybrid (d) BACNi-10, (e) BACNi-20 and (f) BACNi 30 samples

Figure 4

X-ray diffractograms of the pure BAC and hybrid BACNi-10, BACNi-20 and BACNi-30 samples

Figure 5

Experimental and simulated PXRD patterns of the hybrid BACNi-10 sample. The simulated pattern was obtained by structure refinement, considering the contributions of the two indicated phases (Ni and NiO)

Figure 6

$M(H)$ curves recorded at room temperature for the hybrid BACNi-10, BACNi-20 and BACNi-30 samples

Figure 7

MB adsorption process: (a) dispersion of the hybrid BACNi-10 particles in the concentrated MB solution; (b) removal of the hybrid MB-BACNi-10 particles by the magnet

Fitted Surface; Variable: MB solution concentration (ppm)
 2 3-level factors, 1 Blocks, 9 Runs; MS Residual=,8109611
 DV: MB solution concentration (ppm)

Figure 8

Surface Graph of methylene blue adsorption process by hybrid BACNi-X samples