New polyacrylonitrile (PAN)-based porous carbons for the removal of industrial wood dyes from aqueous solutions

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Abstract. Synthetic dyes degradation is a difficult task due to their complex aromatic structure, although its elimination by adsorption is effective. The aim of this research is to produce porous carbons derived from polyacrylonitrile (PAN) as wood dyes adsorbents. PAN is a nitrogen-rich precursor transformed at high temperature into highly porous carbonaceous structure with uniform and size-tunable pores useful for the adsorption of bulky molecules such as dyes. Three types of porous carbons were synthesized: N-doped carbon (P-C), N-doped activated carbon with 4-fold excess of KOH (P-ACT) and N, S-co-doped carbon with sulfur in a 1:1 weight ratio (P-S). Synthesis was performed in two stages: oxidation (280ºC) and carbonization (800ºC). Carbon characterization was performed by different techniques (BET, SEM, EDX, XPS, RAMAN, and pH_{PZC}). Adsorption experiments were conducted on batch mode to study the effect of pH (2, natural and 12), solid/liquid ratio (0.5 and 2 g L^{-1}) and initial concentration (23-27 and 230-285 mg L^{-1}) on the adsorption of a red dye used industrially for preparing dyed wood veneers. Adsorption data were analyzed and well fitted by the pseudo-second-order kinetic model. P-ACT showed the best results of dye removal capacity at all concentrations and pH´s.

Keywords: polyacrylonitrile-based porous carbons, wood dye, adsorption, wastewater

1. Introduction

Many industries have led to the production of huge amounts of colored wastewater (Litefti *et al.*, 2019). Dyeing wastewaters are toxic and carcinogenic to both aquatic life and human beings (Chen and Zhao, 2009). The difficult task of removing dyes can be explained by their highly resistance to degradation due to their complex chemical structures (Zhou *et al.*, 2019). Among conventional dye removal technologies, adsorption is the most common procedure and has been shown to produce the best results for different types of dyes (Cheng *et al.*, 2015). In this respect, the activated carbon is one of the most efficient materials (Al-Degs *et al.*, 2007). Polyacrylonitrile (PAN) is a good polymer precursor for producing carbon materials with a surface area below 3000 m^2 g^{-1} due to its remarkable graphitization degree (Ra *et al.*, 2009). The main reason could be the tightly stacked

and low-defect structure which is formed during the pre-oxidation process of PAN. Additionally, PAN contains nitrogen atoms, which can integrate functionalities into the carbon framework (Kim *et al.*, 2011). Doping with heteroatoms (N, S, B, P, Se) causes structural distortions and changes in the electronic band structure, which alters physicochemical properties. This endows carbon materials with adjustable functions for catalysis, environmental, and energy technologies (Wang *et al.*, 2020). The incorporation of sulfur functional groups to the carbon frameworks can play a dual role, acting both as a morphology stabilizing agent (mild oxidant) and as a dopant, facilitating the formation of N/S-codoped nanocarbons with large specific surface area and precise pore size control (Yuan *et al*., 2019). Moreover, it has been reported that S-doped carbon exhibit an excellent capacity to adsorb heavy metal and enhance the specific capacitance (Shin *et al*., 2007). In addition, physical or chemical activation processes, increase the porosity and specific surface of the porous carbon (Singh *et al.*, 2019). This improvement, together with the surface chemistry of the activated carbon, has a great impact on the adsorption technique. In this work, porous carbons with N and S functional groups were produced from PAN and were applied for the removal of a wood dye.

2. Materials and methods

2.1. Preparation of porous carbons

Three porous carbons were manufactured under different conditions from polyacrylonitrile (Sigma Aldrich) in a tubular furnace (Carbolite): N-doped carbon (P-C), N-doped activated carbon (P-ACT) and N, S-codoped carbon (P-S). P-C was fabricated with polyacrylonitrile powder which was heated under O_2 (10 mL min^{-1}) to 280ºC and stabilized at this temperature for 1 h. Then, the stabilized sample was further carbonized at 800ºC for 0.5 h under nitrogen gas flow (10 mL min^{-1}), followed by free cooling to room temperature. P-ACT was prepared by mixing P-C with a 4-fold excess of KOH (86.2%, Fisher Scientific), heated under N_2 (10 mL min^{-1}) to 800ºC and kept at this temperature for 2 h. P-S was fabricated by mixing PAN with sulfur (Sigma Aldrich) in a 1:1 weight ratio, heated under N_2 (10 mL min^{-1}) to 280ºC, and stabilized at this

temperature for 1h. Finally, the carbon was heated under N_2 (10 mL min^{-1}) to 800 ºC and held at this temperature for 0.5 h, followed by free cooling to room temperature. In addition, commercial activated carbon was purchased in Sigma Aldrich as a reference material for adsorption experiments.

2.2. Adsorbents Characterization

Nitrogen sorption isotherms and textural properties of the carbon were determined by nitrogen physisorption at 77.6 K with ASAP 2020 Micromeritics. The surface area was calculated by the BET method from adsorption data in the partial pressure (p/po) range of 0.04-0.2 and the total pore volume was determined from the amount of nitrogen adsorbed at a relative pressure of 0.99 (Table 1). The morphological features of the adsorbents were examined by scanning electron microscopy (SEM), the images were obtained using a ZEISS FESEM ULTRA Plus with EDX. Raman spectra were obtained using a Raman spectrometer (RENISHAW, InVia Reflex) with a laser ion Ar 514 nm. The chemical nature and atomic quantity of the functional resulting from pyrolysis treatments was studied by X-Ray photoelectron spectrometry (XPS). PHI 5000 Versa Probe instrument (Physical Electronics) equipped with an Al Kα radiation (1486.6 eV) X-ray was used to carry out the XPS analysis. The point of zero charge (pH$_{PZC}$) was determined following the method proposed by Rivera-Utrilla *et al*., (2001).

2.3. Dye

An industrial acid wood dye Red GRA-200% was used for adsorption experiments. The solutions were prepared by dilution with distilled water from a stock aqueous solution of 500 mg L^{-1}.

2.4. Adsorption kinetic experiments

For the study of adsorption kinetics with red wood dye, several batch experiments were conducted in 25 mL Erlenmeyer flasks. The suspensions were shaken with an orbital mini shaker (VWR, Cienytech) at 400 rpm at room temperature (25 ± 1ºC) for different times (0.003, 0.25, 0.5, 1, 3, 24, 48 h). Kinetic experiments were carried out at different pH (2, natural (6.2), 12), solid/liquid ratios (0.5 and 2 g L^{-1}), and initial dye concentration (23-27 and 230-285 mg L^{-1}). Finally, samples were centrifuged (Alresa Microcen) at 9000 rpm for 6 min. The supernatant was removed and analyzed immediately with a UV-Vis spectrophotometer (V-630 Jasco). The residual dye concentration on the supernatant was determined from the calibration curve by measuring the absorbance at the λ_{max} previously determined. All the experiments were performed in duplicate. For comparison, experiments in the same conditions were performed with the commercial activated carbon. The amount of dye adsorbed into porous carbon at time t, or adsorption capacity, q_t (mg g^{-1}), was calculated by the following mass balance relationship:

$$q_t = \frac{(C_0 - C_t) V}{m} \quad [1]$$

where C_0 is the initial dye concentration (mg L^{-1}), C_t is the dye concentration at any time t, V is the volume of solution (L) and m is the mass of adsorbent (g of oven dried (o.d.) carbon). The dye removal efficiency was determined as:

$$\% \ Adsorption = 100 \frac{C_0 - C_t}{C_0} \quad [2]$$

Dye kinetic adsorption was described using Lagergren´s first order (eq. 3) (Lagergren, 1898) and Ho's pseudo-second-order model (eq. 4) (Ho and McKay, 1999).

$$log(q_e - q_t) = log(q_e) - \frac{k_1}{2.303} t \quad [3]$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad [4]$$

Where q_t and q_e are the amounts of dye adsorbed (mg g^{-1}) at t and equilibrium time (h), respectively. The k_1 (h^{-1}) and k_2 (g mg^{-1} h^{-1}) represent the rate constants for pseudo-first and pseudo-second order models, respectively. The adsorption mechanism was also described by the intra-particle diffusion model (eq. 5) (Weber and Morris, 1963).

$$q_t = K_{id} t^{1/2} + I \quad [5]$$

where I (mg g^{-1}) is the intercept and K_{id} is the rate constant of intra-particle diffusion (mg g^{-1} h$^{-1/2}$).

1. **3. Results and discussion**

3.1 Adsorbent Characterization

3.1.1. Structural characteristics of porous carbons

Nitrogen sorption isotherms of P-C and P-S are type I isotherms according to the IUPAC. P-ACT presents an isotherm that can be described by a combination of types I and IV (Li *et al*., 2019) indicating the fabrication of a microporous material (pores < 2 nm) with a high development of mesoporosity (2-50 nm). The commercial activated carbon presents type II isotherm adsorption which is characterized by mainly mesoporous and macroporous structure with surface heterogeneity.

SEM showed that PAN-C is formed by large and compact globules with rough surface and the P-S structure consists of highly vesiculated particles with a diameter between 100-150 nm and a regular shape. Conversely, P-ACT has a highly heterogeneous structure with large globules, zones with irregular macroporosity, and sites with microporosity generated by the activation with KOH. The commercial activated carbon exhibits a sponge-like framework with a disordered structure.

Raman spectra showed two bands around 1350 and 1590 cm^{-1}, which are the D-band and G-band of C, respectively. D-band represents the disorder carbon, and the G-band is related to the graphitic carbon (Li *et al*., 2019)

Table 1. Textural properties and chemical composition of PAN-based porous carbons.

Sample	Textural properties		Chemical composition (%)				Chemical properties
	S_{BET} (m² g⁻¹)	V_{total} (cm³ g⁻¹)	N	C	O	S	pH_{PZC}
P-C	37.5±1.2	0.018	10.5	85.0	4.5	-	8.3
P-S	150.5±3.4	0.189	15.6	78.5	3.2	2.7	8.2
P-ACT	3184.6±41.8	2.114	1.7	84.4	13.9	-	8.1
Commercial C	1059.9±7.8	0.953	-	96.0	4.0	-	7.4

3.1.2 Chemical properties of porous carbons

XPS analysis was performed to determine the presence of functional groups of N and S. C1s spectra of all carbons showed Csp^3 (284.70-285.92 eV) and C=O (290.02-291.88 eV). O1s spectra indicate the presence of carbonyl group around 532 eV. N1s spectra of P-ACT showed mixture of pyridine and pyrrole nitrogen (400.84 eV). P-S present three peaks after deconvoluting N1s spectra, pyridinic N (398.20 eV), quaternary N (400.41 eV) and pyridinic oxide (403.01 eV). S2p spectra showed C-S-C (163.86 eV), C=S (165.13) and $C-SO_2-C$ (167.38 eV) (Yuan *et al.*, 2019). The nitrogen was inherited from PAN, while the oxygen was introduced through polymer pre-oxidation, carbonization and activation.

3.2. Adsorption kinetic experiments

For all carbons essayed, the pseudo-first-order model did not apply well to the data with low values of R^2 (data not shown). By the contrary, the pseudo-second order kinetic model explained better the adsorption kinetics. Table 2 shows the corresponding kinetics parameters for the pseudo-second order and intraparticular diffusion models, together the correlation coefficients for those experiments performed in the conditions essayed which led to the best results of adsorption efficiency for each carbon. This result suggested that the overall rate of red wood dye adsorption
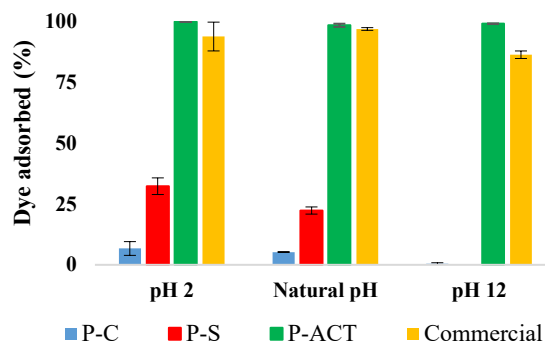

Figure 1. Effect of initial pH on removal efficiency of P-C, P-S, P-ACT, and the commercial activated carbon after 24 h (pH 2, 230 -285 mg L⁻¹, 0.5 g L⁻¹)

could be controlled by chemical processes between dye and carbons. As can be observed in Figure 1, the pH affected the adsorption efficiency for P-C, P-S and commercial activated carbon, obtaining the higher adsorption percentage for acid and natural pH. According to the point of zero charge (Table 1) for the carbons, the experiments carried out at acidic pH, lower than pH_{PZC}, on the surface of the carbons predominate cationic functional groups, whereas at an alkaline pH the carbon surface is negatively charged. Moreover, the red wood dye is a weak acid (pK_a of 10.6), therefore, it is in anionic form in aqueous solution, being better adsorbed on cationic surfaces.

Table 2. Pseudo-second order and intra-particle diffusion kinetic parameters for the removal of red wood dye.

Sample				Pseudo-second-order model				Intra-particle diffusion model					
	Experimental conditions			Removal efficiency	q_t	k_2	q_e	R^2	First stage			Second stage		
	pH	S/L (g L⁻¹)	C_i (mg L⁻¹)	%	(mg g⁻¹)	(g mg⁻¹ h⁻¹)	(mg g⁻¹)		K_{1d} (mg g⁻¹ h⁰·⁵)	I_1 (mg g⁻¹)	R^2	K_{2d} (mg g⁻¹ h⁰·⁵)	I_2 (mg g⁻¹)	R^2
P-C	6.1	2	24	32.8	4.2	0.064	3.6	0.73	0.47	0.27	0.85	-	-	-
P-S	2	2	27	93.0	13.7	0.39	13.7	0.99	13.22	1.051	0.96	0.47	10.80	0.72
P-ACT	1.9	0.5	24	100	52.8	0.19	52.6	0.99	949.25	0	1	0.44	49.25	0.65
	1.9	0.5	285	99.9	602.3	0.026	625.0	1	7497.50	0	1	20.90	514.25	0.69
	6.1	0.5	25	99.6	53.6	0.16	53.2	0.99	941.63	0	0.11	0.02	52.11	0.003
	6.8	0.5	246	100	505.0	0.80	500.0	1	8033.30	0	1	0.89	499.92	0.04
	11.9	0.5	25	99.2	52.8	1.19	52.9	1	16.82	32.47	1	0.04	52.74	0.06
	12.0	0.5	265	100	549.5	0.32	555.6	1	198855	0	1	0.19	556.85	0.15
	2.0	2	24	97.4	13.3	11.77	13.0	0.99	230.10	0	1	0.14	12.32	0.47
	2.0	0.5	250	97.4	556.0	0.032	555.6	0.99	7357.8	0	1	11.73	487.3	0.45
	2.0	0.5	24	97.4	49.3	2.060	49.3	1	113.39	17.24	0.45	0.03	49.68	0.01
Comm. C	6.1	0.5	24	99.2	55.2	0.55	54.9	0.99	827.65	0	1	0.24	53.47	0.17
	6.8	0.5	234	95.9	506.6	0.0044	476.2	0.98	614.97	64.24	0.81	18.85	348.61	0.46
	6.2	2	25	97.3	6.7	2.75	6.6	0.99	16.64	1.74	0.63	0.04	6.35	0.63
	12.6	0.5	25	84.7	49.5	0.26	49.5	0.99	721.16	0	1	0.80	44.47	0.23
	12.2	0.5	259	93.9	545.8	0.012	526.3	0.99	317.18	114.40	0.76	21.05	392.2	0.71

On the other hand, for P-ACT pH did not influence the adsorption capacity. Moreover, this carbon shows the best results in adsorption capacity at all pH´s, even better than the commercial one (Table 2). All kinetic experiments with P-ACT have provided good results, they all achieve maximum adsorption capacity and almost 100% removal of the dye. This is due, probably, to its higher specific surface area (3184.6 m^2 g^{-1}), achieved with the development of the porosity produced (higher total pore volume, Table 2) by activation with KOH. As can be observed in Figure 1, P-C is the carbon with the lowest removal efficiency. Also, its specific surface area and pore volume are the lower of all studied carbons (Table 1), which means that the specific surface area and porosity are directly related to the adsorption capacity. The effect of initial dye concentration, which was varied from 23-27 and 230-285 mg L^{-1}, confirmed that for the P-C carbon at the high dye concentration there is no adsorption due to saturation of the adsorbent. No effect was observed in the rest of the carbons. The diffusion mechanism of P-S, P-ACT, and the commercial active carbon has two simultaneous stages, external mass transfer followed by intra-particle diffusion, as demonstrated by the intraparticular diffusion model.

4. Conclusions

Three porous carbons were fabricated from PAN as an adsorbent for the removal of wood dyes for wastewater treatment. The pH affected the dye adsorption, in general, increasing the adsorption capacity of all carbons at pH 2. The maximum sorption efficiency was attained for P-ACT, even higher than that of the commercial activated carbon, due to the development of porosity and a higher specific surface area. Adsorption kinetics was better fitted by the pseudo-second order model and the intraparticular diffusion model confirmed the existence of external mass transfer followed by intra-particle diffusion. The results of this work have shown that the activated carbon from PAN (P-ACT) provided the best results in the removal of dyes thanks to porosity development and increase of specific surface area in the activation process.

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