

Activated Biochars Used as Adsorbents for Dyes Removal

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Adsorption represents one of the most interesting technique for the removal of pollutants from wastewaters. Activated carbons show the best performances on this kind of processes but their high production costs limit their applications. In this context a big challenge is to find new materials having characteristic similar to those of commercial activated carbons but being environmental friendly and cheaper.

In this work the adsorption efficiency of activated biochars produced from pine wood was investigated on the removal of dyes from water. An innovative method for the activation of the biochar using deep eutectic solvents (DES) was tuned and the characteristics of the obtained adsorbent material were compared with those of biochar activated with traditional method and non-activated biochar.

The best adsorption capacities were obtained with the DES activated biochar, reaching a value of 480 mg/g for the methylene blue adsorption. Adsorption isotherm and kinetic models were applied to experimental data in order to understand the adsorption mechanism of the process.

1. Introduction

Dyes as wastewater pollutants represent a big concern for the environment. The discharge of dyes into water is ascribable to industries such as textile, leather, paper, plastics, etc. Different solutions have been studied to solve the problem of water pollution, such as photocatalysis and adsorption (Scarsella et al., 2017). Adsorption is one of the most used technique for wastewater purification, applied to remove organic molecules at industrial scale due to its low cost and its ease of operation. Among the different adsorbents used for wastewater treatment, activated carbons show the most suitable characteristics, such as high porosity, well-developed internal surface area and high adsorption capacity.

However, the production costs lead to a serious drawback for the use of activated carbons as industrial adsorbents. To overcome this drawback, recent years have seen an increasing interest in the production of activated biochar from biomass, being a renewable and low cost adsorbent material. Biochar is the solid residue of biomass pyrolysis and it is characterized by high porosity and high amount of carbon in aromatic form (de Caprariis et al., 2015). When properly activated, this material presents sorption capacity and surface area similar to that of activated carbon. The activation procedure aims to improve the biochar characteristics needed in the adsorption process. Different methods are available for the activation of biochar. Physical activation consisting in a high temperature treatment in a continuous flow of gas such as CO₂ or H₂O enhances the surface area and porous structure, and thus the sorption capacity for water contaminants. Furthermore, heavily condensed polycyclic aromatic and π -electron rich sites are formed during physical activation providing hydrophobic properties to biochar which leads to enhanced properties for sorbing hydrophobic organic compounds (Manyà, 2012). Chemical activation consisting in the reaction of char with a chemical agent such as an acid or a base leads to the formation of micropores by subsequent dehydration and/or oxidation. Although chemical activation presents some difficulties due to corrosion of the apparatus by chemicals and complicated recovery of chemicals, its much higher efficiency in the activation of biochar with respect to the physical treatment makes its application very interesting.

In the literature many studies on the adsorption of dyes by means of chemically activated biochar are available. The chemical activation is usually performed on the biochar and then the activated material is subjected to an additional thermal treatment (Puccini et al., 2017; Hayatu et al., 2017).

In this work the adsorption capacity of pine wood biochars was tested on the removal of two dyes. The adsorbents were produced by chemical activation of the biomass followed by thermal treatment. Using this

process only one thermal treatment is needed and thus low energy consumptions are used for the production of the adsorbent. The char was activated by treatment with two different basic solutions. One activation was performed with NaOH solution and the other with a basic deep eutectic solvent (DES). DESs are emerging as environmental benign solvents and reagents in many different research fields and are extensively studied for lignocellulosic biomass fractionation (van Osch et al., 2017) and processing (De Oliveira Vigier et al., 2015) or as biomass pretreatment to ease its conversion into value-added products (Loow et al., 2017)

In our knowledge this work reports the first example of a biomass activation treatment performed exploiting the today well known characteristics of DES (Smith et al., 2014). The adsorption capacities of activated biochars were compared with that of thermal biochar produced without activation.

2. Materials and methods

2.1 Adsorbent preparation

Thermal biochar (TB) was produced by the pyrolysis of pine wood biomass ground to pass in 500 μm sieve. The pyrolysis was performed in a quartz tube (2.5 cm ID and 50 cm L) at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ up to 750 $^{\circ}\text{C}$ under a nitrogen flow of 0.2 L/min; the maximum reaction temperature was kept constant for 1 h in order to assure the completion of the reactions.

The biochar activated with NaOH (AB-NaOH) was obtained using a 4 M NaOH solution (pH=12).

The biochar activated with DES (AB-DES) was obtained using a basic DES constituted by glycerol as hydrogen bond donor and potassium carbonate as salt (Naser et al., 2013) in a molar ratio 5:1. The main characteristic of this particular DES is its high pH value (pH 12 at 80 $^{\circ}\text{C}$).

Both biomass activation treatments were performed at 80 $^{\circ}\text{C}$ for two hours, using the same ratio solution volume: biomass mass and following the procedure reported by de Caprariis et al. (2017).

The adsorbent surface areas were evaluated by the measurement of the Iodine number (nI) (Mianowski et al., 2007). The Iodine number was obtained according to the ASTM D 4607-86.

2.2 Adsorption studies

The batch adsorption studies were performed in a set of vials (20 ml) where 15 mL of adsorbate solution was put in contact with the adsorbents (15 mg) in an orbital shaker at a constant temperature of 20 $^{\circ}\text{C}$. The aqueous solutions were prepared with methylene blue and rhodamine b with different concentrations in water ranging between 50 and 1200 mg/L. Equilibrium studies were performed to investigate the sorption capacities of the adsorbents and to carry out the isothermal adsorption curves. The equilibrium tests lasted 24 h and afterwards the suspensions were filtered and the concentration of the two dyes were determined measuring the adsorbance with a UV-visible spectrophotometer (Sequoia-Turner, 340) equipped with a quartz cell having a path length of 1 cm. The concentration of methylene blue dye and rodamine b in the aqueous solutions were measured at $\lambda_{\text{max}} = 664 \text{ nm}$ and $\lambda_{\text{max}} = 544 \text{ nm}$, respectively. The sorption capacity at the equilibrium, q_e (mg/g), was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/l) are the initial and equilibrium concentration of the dye in the solution, respectively, V (l) is the volume of the solution and W (g) is the dry mass of the adsorbent.

Batch kinetic experiments were conducted in the same set-up used for the equilibrium tests, the adsorption capacity as a function of time, q_t (mg/g) was calculated as:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

Where C_t (mg/l) is the dye concentration at time t .

2.3 Isotherm adsorption and kinetic models

Adsorption isotherm are fundamental to understand the adsorption mechanism and thus to be able to design the adsorption system. In this study two adsorption isotherm models were taken into consideration, Langmuir (Langmuir, 1918) (Eq.(3)) and Freundlich (Yan et al., 2008) (Eq.(4)).

$$q_e = \frac{Q_m K_L C_e}{1 + K_L C_e} \quad (3)$$

$$q_e = K_f C_e^{1/n} \quad (4)$$

where Q_m (mg/g) is the maximum adsorption capacity, K_L (l/mg) the Langmuir constant K_f and n (l/mg) the Freundlich constants.

Kinetic models are essential to determine the rate of adsorption process and to give important information on the reaction mechanism. Two kinetic models, the pseudo-first order (Ncibi et al., 2007) (Eq.(5)) and the pseudo-second order (McKay and Ho, 1999) (Eq. (6)) were applied to the experimental data.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

where k_1 (1/min) and k_2 (g/mg min) are the rate constant of pseudo-first and pseudo-second order adsorption kinetic model.

3. Results and discussion

In Table 1 the Iodine numbers of the biochars are reported. The Iodine number measurements point out that the activation procedure has a great influence on the material surface area. In fact, after the activation procedure the Iodine number is doubled. The activation with DES produces the biochar with the highest surface area which presents value close to those of commercial activated carbon (800-1000 mg/g).

Table 1: Iodine numbers of the three tested biochars.

Samples	nl (mg/g)
TB	380
AB-NaOH	552
AB-DES	645

In Figure 1 the adsorption capacity at equilibrium is reported for the three adsorbents. The char activated with DES has a slightly higher adsorption capacity in the case of methylene blue while in the adsorption of rhodamine b the effect is more visible. It is evident, as expected, that the activation produces a great enhancement of the adsorption capacity of the biochar due to the major surface area which is a key factor in this kind of processes. The capacity of adsorption of methylene blue is much higher than that of rhodamine b, probably owing to steric factors and to biochar surface functional groups, being both the dyes basic dyes.

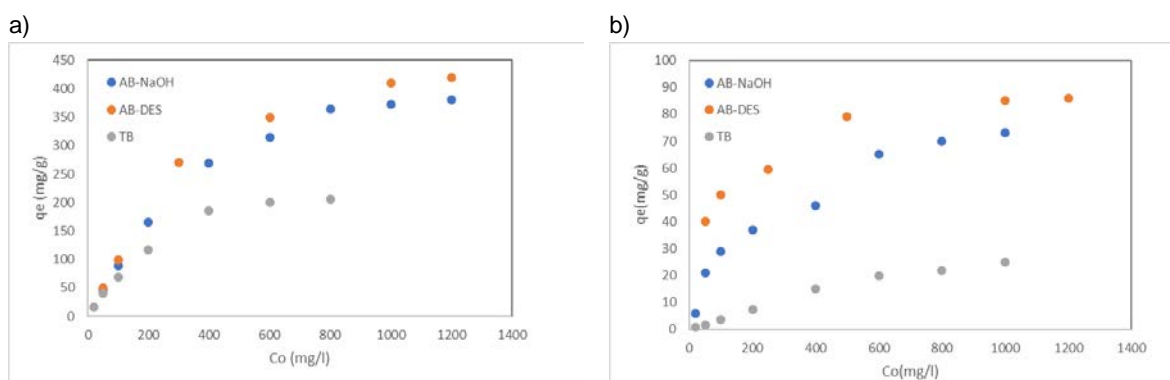


Figure 1: Adsorption capacities as a function of the initial dye concentration of the three biochars a) with methylene blue solutions; b) with rhodamine b solutions.

The fit of the adsorption isotherm models in the linearized form is shown in Figure 2. For the methylene blue the sorption isotherms were all quite well simulated by the two models with a $R^2 > 0.95$ when thermal biochar and biochar activated with NaOH were used. This suggests that not a unique mechanism of sorption explain this behaviour. Nevertheless, for the biochar activated with DES, the adsorption data fit the Langmuir model

and thus a clear monolayer adsorption is observed. For the rhodamine b the two isotherm models fit well the data with R^2 always greater than 0.95, suggesting that the adsorption takes place as a combination of different mechanism.

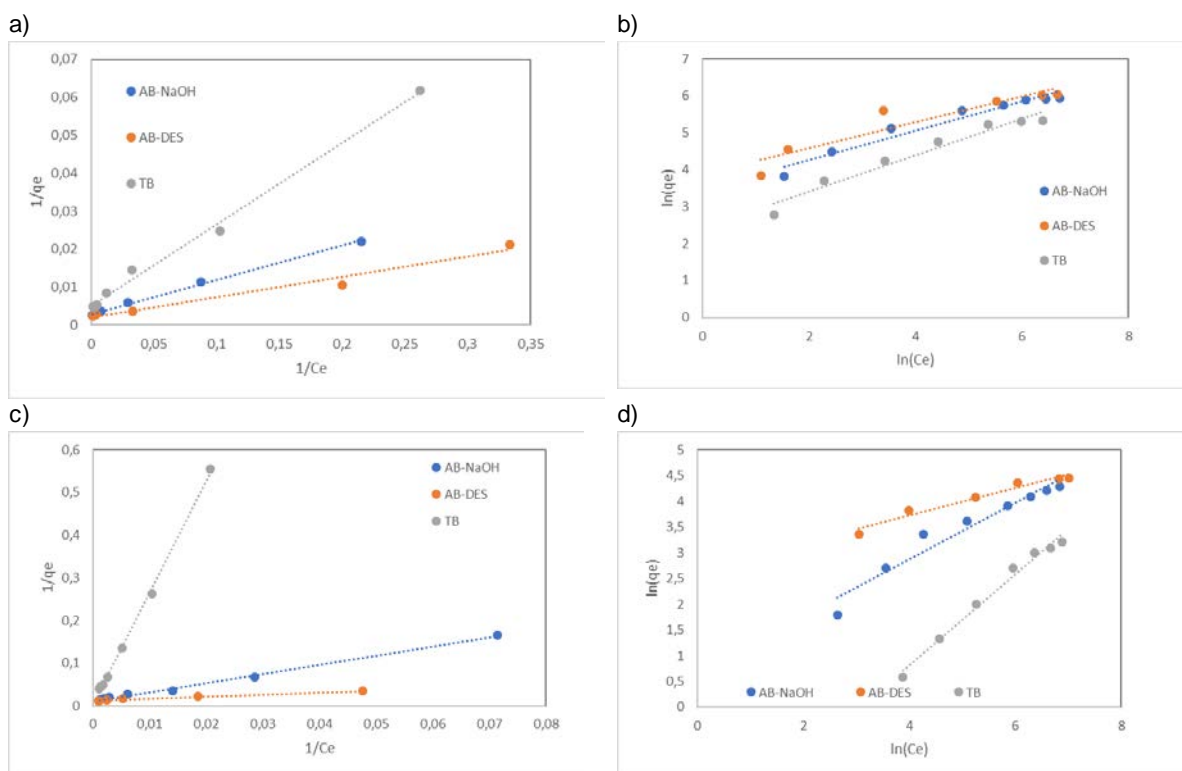


Figure 2: Fit of the adsorption isotherms a) Langmuir model methylene blue b) Freundlich model methylene blue c) Langmuir model rhodamine b d) Freundlich model rhodamine b.

Table 2 shows isotherm constants and correlation coefficients for the different adsorbents. The maximum adsorption capacity values obtained fitting the data with the Langmuir model indicate that the biochar activated with DES presents the best performances in the adsorption of methylene blue. Considering the Freundlich model, k_f is taken as a relative indicator of sorption capacity confirming the results of the Langmuir model fit. Furthermore, all the values of n are greater than 1 indicating the favourability and capacity of the adsorbent/adsorbate system especially in the case of methylene blue.

Table 2: Isotherm constants for the sorption process onto the four adsorbents.

Samples	Adsorbate	Langmuir model			Freundlich model		
		Q_m	K_L	R^2	k_f	n	R^2
TB	MB	200	43	0.994	11	2.0	0.957
AB-NaOH		452	31	0.997	33	2.5	0.951
AB-DES		680	25	0.974	49	2.8	0.878
TB	Rb	65	12	0.998	14	1.1	0.957
AB-NaOH		82	7.5	0.995	19	1.8	0.986
AB-DES		95	4.8	0.981	21	1.1	0.968

The influence of contact time on the sorption of the two dyes onto the studied adsorbents is shown in Figure 3 for an initial solution concentration of 600 mg/l. The adsorption process is very fast, after the first 30 minutes the 80 % of the total adsorption capacity was already reached. The sorption then gradually levelled off to equilibrium within about 4 h.

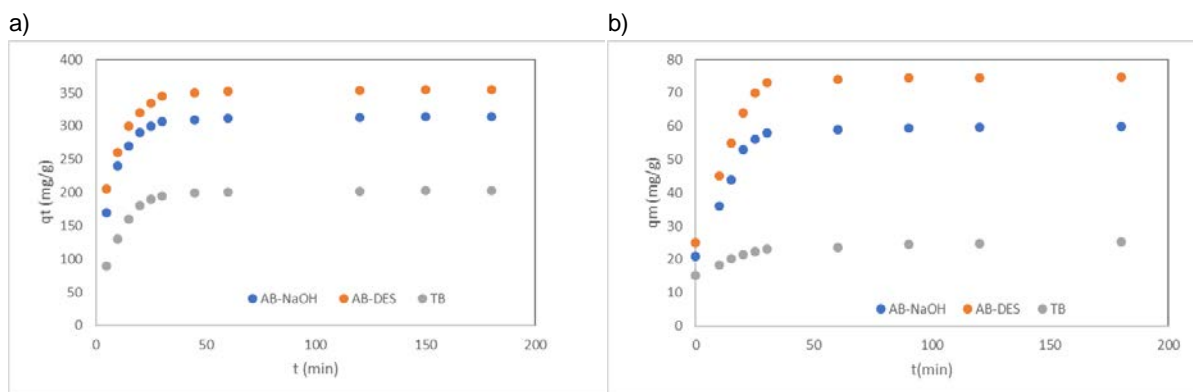


Figure 3: Effect of contact time on the adsorption process for the three tested adsorbents a) methylene blue b) rhodamine b.

The adsorption processes tested follow the pseudo-second order kinetics as expected. The pseudo-second-order kinetic model indicates that the rate limiting step may be the surface adsorption interactions, and also that the adsorption capacity is proportional to the number of active sites of pyrolytic biochar (Franca et al., 2009).

Table 3: Kinetic parameters of pyrolysis wastewater organic pollutant onto different adsorbents.

Samples	Adsorbate	Pseudo first order			Pseudo second order			
		qe,exp	k1	qe	R ²	k2	qe	R ²
TB	MB	201	0.010	172	0.932	0.002	203	0.992
AB-NaOH		315	0.012	356	0.947	0.004	326	0.989
AB-DES		350	0.024	337	0.961	0.007	361	0.998
TB	Rb	25	65	16	0.974	0.0009	27	0.994
AB-NaOH		59	82	75	0.921	0.001	58	0.998
AB-DES		77	95	86	0.945	0.005	79	0.991

4. Conclusions

Activated biochars produced from pine wood were tested on the adsorption of two different dyes, methylene blue and rhodamine b. An innovative method for the activation of biochar using deep eutectic solvent was investigated and the results in terms of adsorption capacity were compared with the results obtained with a biochar produced by thermal treatment and a biochar activated with NaOH solution. The use of DES in the activation process leads to increased surface area of the adsorbent materials and as a consequence greater adsorption capacity of about 20 % for both the tested dyes. All the produced biochars present much higher sorption activity for methylene blue than for rhodamine b.

The kinetics of adsorption on biochars and activated biochars follow a pseudo-second-order kinetic model indicating that surface adsorption is the rate-limiting step. Furthermore, the Langmuir and Freundlich models provided good fitting for all the tested materials indicating that a unique adsorption mechanism can not be individuated.

The use of deep eutectic solvents seems to be a very interesting method to produce activated biochar with very high adsorption capacity and could represent a new low cost and environmental friendly technique for the synthesis of biochar that can be used as substitute of activated carbon in the adsorption processes in the waste water treatments.

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