Activated Carbon from Biomass from $Zncl_2$ Activation for Methylene Blue Adsorption

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Received: 01/08/2023; Accepted: 01/10/2023 Published: 15/12/2023

Abstract
Investigations were conducted on activated carbons derived from the plentiful natural resource of Zizyphus lotus L seeds for the purpose of eliminating methylene blue from aqueous solutions. These activated carbons were synthesized through chemical activation using zinc chloride under various conditions, aiming to achieve carbons characterized by elevated porosity. An essential parameter influencing the porous structure of the resulting charcoal was the carbonization temperature. Through SEM analysis, the activated carbons were thoroughly characterized, and BET specific surface area analysis was employed to estimate pore volume and surface area. The activated carbons exhibited surface areas (S_{BET}) and micropore volumes approximately measuring 313.53 m^2/g and 0.108519 cm^3/g, respectively. Notably, the developed activated carbon displayed a considerable capacity for adsorbing methylene blue from aqueous solutions.
Keywords: Activated carbon; Zizyphus lotus Lseeds; Surface area; Chemical activation; methylene blueremoval.

Tob Regul Sci. ™ 2023 ;9(2): 1828-1835
DOI: doi.org/10.18001/TRS.9.2.116

1. Introduction

Adsorption is an effective and widely used process in advanced wastewater treatment, particularly for removing traces of hazardous organic and inorganic substances. Activated carbon is a commonly used adsorbent due to its high specific surface area, porous structure and chemical reactivity. The process involves pollutants adhering to the surface of the activated carbon, forming a

thin layer on its surface[1]. Depending on the mechanisms that determine how the substances are retained by the activated carbon. Adsorption on activated carbons can be categorized into two

main types: chemisorption (or chemical adsorption)[2] and physisorption (or physical adsorption)[3],[4].

A great deal of research has been carried out to explore the preparation of activated carbons from agricultural waste[5],[6],[7],[8],[9],[10].

Activated carbon preparation involves two distinct processes: physical activation and chemical activation. In contrast to physical activation, chemical activation provides two significant advantages, 1) the process operates at a lower temperature, offering benefits from both an energy and operational standpoint. 2) chemical activation typically achieves higher overall efficiency[11].

Chemical activation is recognized as a preparatory method that involves the use of chemical agents, usually substances containing alkali and alkaline-earth metals, along with certain acids such as KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $ZnCl_2$, $MgCl_2$,H_3PO_4 and H_2SO_4[12],[13],[14],[15],[16],[17],[18].

Synthetic dyes play an important role in the textile and dyeing industry, and their use, like that of many chemicals, presents potential risks.As cationic dyes have proved to be more toxic than anionic dyes, their removal from the aqueous environment is of greater importance[19].

Methylene Blue (MB) dye can cause eye burns and permanent damage in humans and animals. Inhalation may result in brief episodes of rapid or labored breathing, while ingestion may cause burning, nausea, vomiting, profuse sweating, mental confusion, painful urination and methemoglobinemia[20].

The present study aimed to chemically activate carbon (AC) from Zizyphus lotus L seedsusing $ZnCl_2$ and investigate its effectiveness in adsorption studies for methylene blue (MB) dye removal.

2. Materials and methods

2.1. Raw material

Zizyphus lotus L seeds were sampled in Biskra city, in Algeria. The seeds underwent a series of treatments, including: washing with distilled water, drying at 110°C in an oven for 24 hours, grinding and granulometric separation into particles with diameters ranging from 1 to 2 mm.

2.2. Preparation and characterization of activated carbon

The activation process was carried out in an impregnation ratio (1:2) of $ZnCl_2$ (2 M) and particles. The mixture was kept under magnetic stirring for 1.5 hour, then placed for drying at 110°C for 24 hours. The dried mixture was divided into three, placed in a muffle furnace, and the three activated carbons are obtained, at 400°C (AC1), 500°C (AC2) and 600°C (AC3) respectively met, and held for 1 hour. After cooling, the resulting ACs were washed several times with HCl (0.1 mol/L) and hot distilled water (to pH 6-7) to remove waste activating agent and by-products produced during the process.

The textural characteristics of the activated carbons were assessed through N2 adsorption-desorption isotherms at 77 K, employing a surface analyzer. The surface area was determined utilizing the Brunauer-Emmett-Teller (BET) method.

Scanning electron microscope (SEM) images were acquired to investigate the morphologies of the three prepared activated carbons (ACs). Additionally, the functional groups present in these ACs were analyzed using Fourier-transform infrared (FT-IR) spectra, recorded in the range of 4000 to 400 cm^{-1}.

2.3. Batch adsorption studies

The cationic dye, methylene blue (MB), which was used as adsorbate, has a molecular weight of 319.85 g/mol and a molecular formula of $C_{16}H_{18}N_3SCl$.

For adsorption studies, a stock solution of MB 20 mg/L was prepared by dissolving an appropriate amount of dye in distilled water. Adsorption equilibrium studies were carried out using 50 ml solutions with different concentrations of MB (5-20 mg/L), which were placed in contact with 0.5 g AC, and agitated for 60 min under cover. The mixtures were then filtered to minimize the effects of particles suspended in the solution.

3. Results and discussion

3.1. Yield and textural characterization of adsorbent

$ZnCl_2$ as an activating agent can be attributed to its depolymerising effect on biopolymers. This effect induces dehydration and redistribution, facilitating the transformation of aliphatic compounds into aromatic compounds, which increases the overall yield of ACs[21],[22]. Seeds activation occurs as a result of cellulose and lignin breakdown within the temperature range of 250 to 350 °C and 250 to 500 °C, respectively. The subsequent phase, spanning from 500 to 600 °C, is attributed to the vaporization of zinc chloride, where the elevated temperature causes the evaporation of zinc chloride, given that its melting and boiling points are 318 and 600 °C, respectively[23].

Most of the activated substance is carbon, over 66% in all three variants. It is clear that the carbon content increases as the activation temperature increases. According to the table, the "burn-off rate" is proportional to the activation temperature, reaches a maximum value of 66.98% for variety 67.98 AC1, % for variety AC2 and 68.68% for variety AC_3.

Table 1: The physical and chemical characteristics of the three ACs

activated carbon	AC1	AC2	AC3
Yield of Activated Carbon%	43.33	39.33	29.87
Bulk density (g/cm^3)	0.563	0.533	0.435
Humidity content H %	4.6	3.66	2.02
C (%)	66.98	67.98	68.68
O (%)	31.02	28.27	29.15
BET surface area (m^2/g)	39,6175	214,5882	313,5330
BJH Adsorption Average pore diameter (4V/A), (nm)	64,0565	12,6647	2,7802
BJH Desorption average pore diameter (4V/A), (nm)	--	17,9559	--

3.2. Surface chemistry and morphological characterization of materials

We have plotted infrared spectra of the raw material (RM) and the three types of ACs on the (Fig 1), Changes in the chemical functional groups serve as indicators of the modifications undergone during activation facilitated by the activating agent and the subsequent carbonisation process. The predominant type of bond, O-H in alcohols, is characterised by its robust and broad nature. Throughout the chemical activation process, the O-H groups undergo changes as they are targeted, leading to alterations in the adsorption bands linked to the decrease in O-H vibrations. This phenomenon explains the complete using of oxygen during the pyrolysis process, ultimately contributing to the formation of a porous structure on the substrate.

In addition, the carbons exhibit asymmetric N-O stretching (associated with nitro compounds), which manifests itself as a strong bond in the frequency range from 1550 to 1475 cm^{-1}[24].

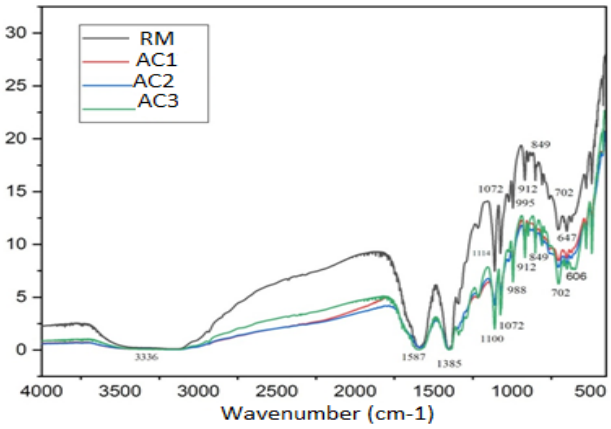

Fig 1: FT-IR spectra of the RM and thethree obtained ACs

(Fig 2) depicts the microscopic examination conducted on various activated carbons. An observable increase in porosity is evident when transitioning from AC1 to AC3, manifesting as surface heterogeneity. The SEM micrographs further illustrate the filamentary structure of the carbons, marked by dotted illumination and significant porosity. The heightened surface heterogeneity implies an increased potential for improved adsorption performance by the material[25], [26].

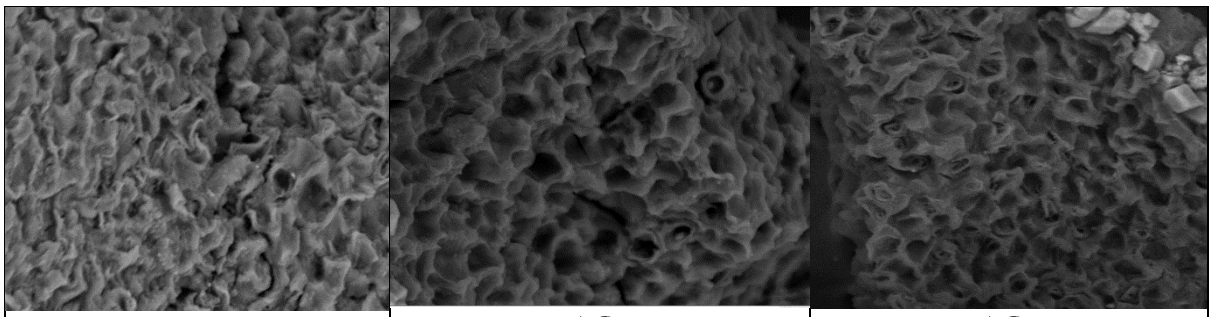

Fig 2: SEM images of the three obtained ACs

3.4. Adsorption of MB

3.4.1. Influence of contact time on the adsorption of Methylene Blue

The absorption dynamics of methylene blue in aquous solution with a concentration of 20mg/l, using 0.5g of activated carbon, indicate that a significant amount of methylene blue is absorbed within the initial 2 minutes (Fig 3) for the three ACs[27].

The findings indicate that the enhancement in decolorization efficiency rises as the contact time increases. This phenomenon can be elucidated by considering the kinetics of the reaction, specifically the migration and transfer of BM dye molecules from the solution to the surface of the adsorbent. This migration is driven by the influence of distribution and dispersion forces[28].

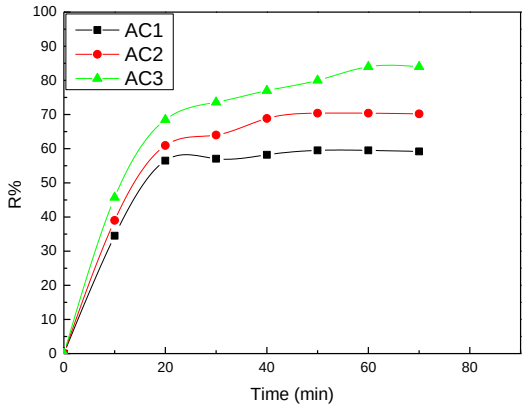

Fig 3: Effect of contact time on methylene blue removal efficiency

3.4.2. Effect of Amount of ACs

The impact of the quantity of adsorbent on the removal of methylene blue was examined. Throughout the experiments, the initial concentration of the methylene blue solution was consistently maintained at 20 mg/L, with an initial volume of 50 ml. The mass of carbon varied within the range of 0.1 g to 0.6 g [29]. The outcomes illustrated in Fig 4 reveal a notable rise in removal efficiency as the quantity of activated carbon increased, reaching a peak at 0.5 g. Subsequently, there were no significant changes in removal efficiencies with further increases in the quantity of the adsorbent. This is explained by the fact that an increase in mass leads to an increase in specific surface area, thereby providing numerous active sites.

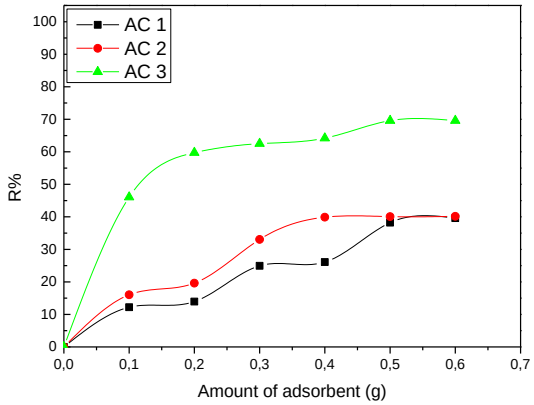

Fig4 :Effect of adsorbent amount on the removal of methylene blue

3.4.3. Effect of initial concentrationof Methylene Blue on adsorption

To assess the impact of Methylene Blue concentration on the adsorption process with activated carbon, we conducted experiments by diluting the initial solution (C_0=20 mg/l) into four daughter solutions with distinct concentrations (5mg/l; 10mg/l; 15mg/l and 20mg/l), each in a 50ml volume Subsequently, 0.5g of activated carbon was added to each solution under stirring for 1 hour at room temperature.

It can be seen that the removal efficiency of the pollutant decreases as the concentration increases. This is because when the concentration decreases, the free ions in the solution also decrease. As a result, the competition for binding between the positively charged ion and the active sites forming the adsorption material becomes greater, which facilitates binding.

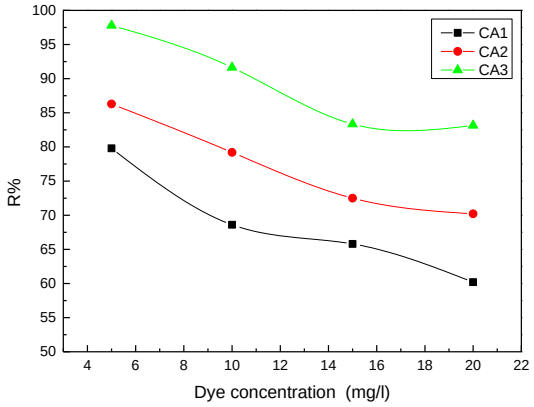

Fig 5: Effect of dye concentrations on the R% adsorbed.

4. Conclusion

Chemical activation using $ZnCl_2$ on material derived from Zizyphus lotus L seedsyields activated carbons with specific surfaces ranging from 39,6175 to 313,5330 m^2/g. The morphological changes of the material post-activation were examined through SEM images. Surface group analysis via FT-IR indicated the removal of certain groups with increasing pyrolysis temperature, likely

corresponding to oxygenated groups and aromatic rings on the surface of ACs. These features potentially facilitate the interaction between methylene blue dye and ACs. The conducted methylene blue dye adsorption studies yielded satisfactory experimental data. Consequently, the findings from this investigation lead to the conclusion that Zizyphus lotus L seedsholds promise as a potential precursor for activated carbon.

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