Removal of methylene Blue Using Adsorption onto Activated Carbon Derived From juniper berries

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Abstract

The present study reports the preparation of three activated carbons produced from Juniperus berries, using KOH as activating agent and its ability to remove Methylene Blue from aqueous solutions.The work aimed to examine how varying carbonization temperatures impact the pore structure of activated carbon and were selected in the range of 400–600 °C.Several physical properties have been calculated, such as Bulk density, Humidity contentand,Burn-offfor obtained activated carbons, and characterized byN2 adsorption–desorption isotherms at 77 K, BET, SEMand CHNS. The results show that activated carbons presents microporous features with BET surface area which were determined by application of the Brunauer–Emmett–Teller (S_{BET})was achieved 145.8329 m2/g. We examined the impact of different experimental variables, including adsorbent quantity and initial dye concentration. Maximum dye removal of 69.59% isobtained for the activated carbon prepared at 600°C.

Keywords: Activated carbon, Chemical activation, Juniperusberries,Textural characterization, adsorption

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1. Introduction

The control of pollution has become one of the primary areas of scientific activity, particularly concerning water pollution[1]. This issue is a significant concern in many industries due to the discharge of untreated or inadequately treated wastewater[2]. One significant source of water pollution is the use of dyes to color products in various sectors, including pharmaceuticals[3], leather[4], food[5], paper[6], cosmetics[7], and the textile industry by itself consumes more than 107 kg of dyes per year[8]. This poses substantial challenges for environmental regulatory agencies and can have a detrimental impact on the aquatic ecosystem, even at very low concentrations, rendering water unsuitable for various purposes[9]. Dyes are classified into various categories according to their ionic charges, which encompass anionic dyes

(such as direct, acid, and reactive dyes), cationic dyes (comprising basic dyes), nonionic dyes, and zwitterionic dyes[10].

Methylene Blue is the most important basic dye discovered in 1878, It is widely used, While methylene blue is not highly dangerous, it can lead to adverse effects. A sudden exposure to methylene blue in humans can result in an elevated heart rate, shock, vomiting, cyanosis, the formation of Heinz bodies, tissue necrosis and jaundice[11].

Dye decolorization is critical step in wastewater treatment There are several methods employed for efficient dye removal Coagulation-flocculation, Oxidation processes, Biological Treatment, Membrane-based methods and Adsorption[12].

Adsorption can be classified as either physical or chemical depending on the nature of the forces involved. When adsorption occurs without any chemical reaction, brought about by Van der Waals forces, it is generally referred to as physical adsorption, or physisorption. The phenomenon is called chemical adsorption, or chemisorption. If it involves electron sharing between the adsorbate molecules and the surface of the adsorbent, the adsorbate undergoes a chemical interaction with the adsorbent. It is typically limited to a single layer of molecules on the surface[13,14]. TheseTechniques using materials like zeolites, activated carbon…

Activated carbon derived from wastes materials presents an eco-friendly and sustainable approach to waste management. Among the common agricultural waste sources suitable for activated carbon production, the following are prominent: coconut shell [15], Dates' Stone[16], rattan sawdust[17], Ziziphusjujuba cores[18], buriti shells[19]and bamboo dust [20].

Many trees are abundant in seeds or fruits, and one of these trees is the genus Juniperus[21], which is a part of the Cupressaceae family and includes around 67 species worldwide. In Algeria, the flora contains five of these species[22]. The species of Juniperusis considered as an important medicinal plant largely used in traditional medicine. The seed decoction of Juniperus is used as folk medicine for kidney diseases, and as a diuretic and abortive in Uzbekistan[23].

2. Materials and methods

2.1. Materials

To promote the utilization of local materials for activated carbon production, we employed juniper berries from the northeastern region of Algeria (Batna), an area renowned for its abundant juniper trees.Methylene Blue (MB) was used as an adsorbate in this stady. his molecular formula of $C_{16}H_{18}N_3SCl$ (Fig. 1) and molecular weight of 319.85 g/mol[24],To prepare all the solutions and reagents, distilled water was used as the solvent.

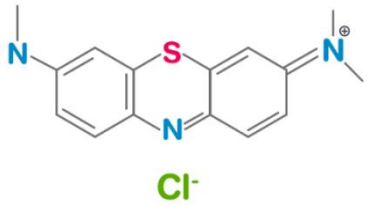

Fig. 1. Structure of Methylene blue

2.2. Preparation of activated carbons derived from Juniperusberries

Raw material (Juniperus berries) used for preparation of activated carbon was procured locally, washed, dried, crushed to desired mesh size (0.5-2 mm). The product was then impregnated with potassium hydroxide (KOH) in a 1:1 impregnation ratio, for 6 h continuous agitation, the mixture was dried at 110 °C for 24 h.

After that, the obtained impregnated samples were exposed tocarbonization process at 400, 500 and 600°C for 2 h, at a heating rate of 5 °C/min, after carbonization process, the samples were washed several times with hot water, and finally with cold water to remove residual chemicals impurities and reduce ash contents of the activated carbons. The obtained activated carbons were dried at 110°C for 24 h.

The activated carbons produced with KOH activation at 400, 500 and 600°C were denoted as AC1, AC2 and AC3, respectively.

Activated carbons were prepared and characterized and used as adsorbents for the removal of methylene blue (MB) from aqueous solutions.

2.3. Characterization of activated carbons

The ash content was determined according to a standard method [25]. The bulk density was determined following the protocol [26]. Moisture content was determined using the oven drying method[27]. The calculation equations are provided in Table 1.

Table 1 Textural properties and yield of ACs activated by KOH

activated carbon samples	AC1	AC2	AC3
Carbon yield % =. (m1 / m0) ×100	39.70	37.27	30.17
Bulk density = m/v (g/ml)	0.459	0.467	0.432
Humidity content H % = [(m0-mf)/m0] × 100	4.0	3.4	3.2
Burn-off %=[(mi-mf)/mi]×100	53.27	53.99	77.5
C (%)	79.961	80.93	86.10
O (%)	10.77	11.03	9.05
H(%)	7.906	4.595	4.740
BET surface area (m^2/g)	3.1736	3.1587	145.8329
BJH Adsorption Average pore diameter (4V/A), (nm)	6.1541	7.1536	9.1933
BJH Desorption average pore diameter (4V/A), (nm)	7.5171	10.0463	

A measurement of specific surface areas of the activated carbons produced from the waste biomass has been made by N2 adsorption at 77 K (Fig. 2), The activated carbons were analyzed for carbon, nitrogen, hydrogen, sulfur, and oxygen abundances using CHNS. The characteristics of the activated carbons are presented in Table 1.

AC 1 AC2 AC3

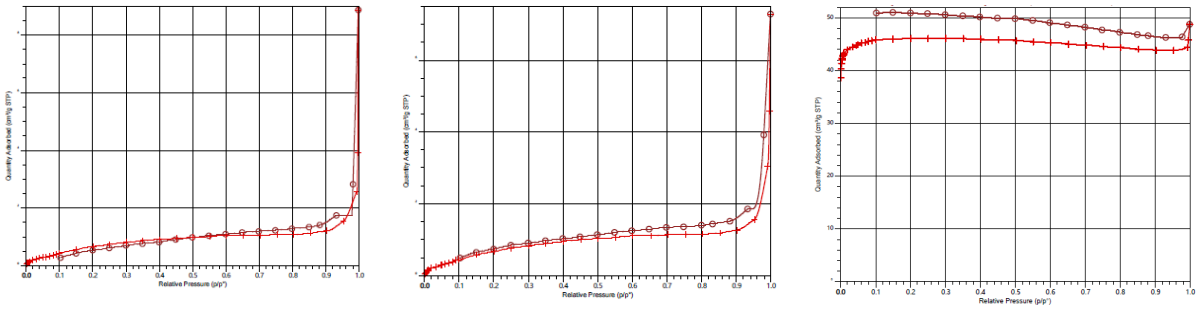

Fig. 2. N2 adsorption and desorption isotherms at 77 K of AC1, AC 2 and AC3

The surface morphologies of the activated carbon materials were investigated with a emission scanning electron microscope (SEM) as shown in (Fig .3).

AC 1 AC 2 AC 3

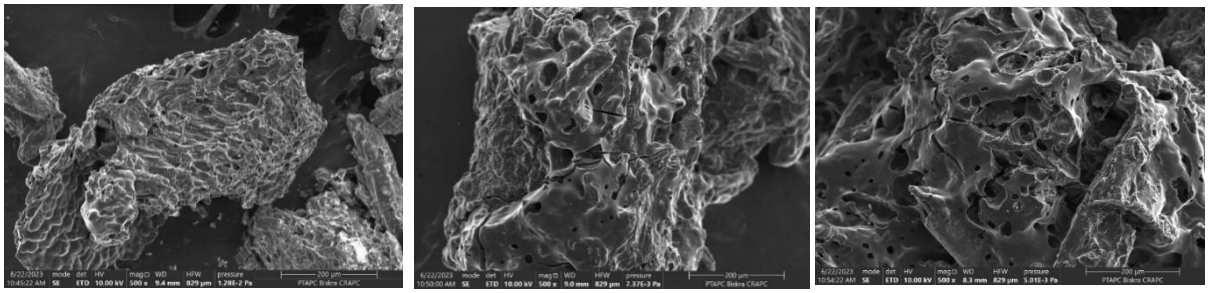

Fig.3. SEM images of AC1, AC 2 and AC3

2.4. Adsorption experiments

A 20 mg/L solution of Methylene Blue (MB) was prepared as a stock solution for future experiments, and then diluted as necessary. Parameters influencing adsorption, such as the initial adsorbate concentration, contact time, and the mass of the adsorbent, were investigated in different sets of batch adsorption experiments.

After equilibration, the samples were filtered, and the concentration of MB determined with a UV–Vis spectrophotometer at 664 nm. The percent dye removal equilibrium adsorption (Re %) at any time was determined by the equation:

$$R\ (\%) = [(C0 - C\ e) / C0] \times 100$$

Where C0 is the initial MB concentration (mg/L),

Ce is the equilibrium MB concentration (mg/L).

3. Results and discussion

3.1. Characterization of Activated carbons

The proximal and ultimate analysis results for the obtained were displayed in Table I. The prepared activated carbons exhibit significant carbon content. This can be attributed to the activating agent functioning as a dehydrating agent, influencing pyrolytic decomposition and preventing the formation of ash, consequently enhancing the carbon yield. Other elements, including oxygen content, varied, potentially leading to diverse chemical characteristics in the activated carbon, resulting in the formation of various functional groups[26].

The surface and pore structure of porous materials play a crucial role in adsorption processes, as this is where chemisorption and/or physisorption take place. The micropore volume values in the table indicate that charcoal pyrolyzed at 600°C falls within the microporous range. Furthermore, the surface area exceeded that of activated carbons prepared at 400 and 500°C. This observation illustrates the impact of temperature elevation on the specific surface area of the activated carbon[18], Through the figure, we observe that the higher the activation temperature, the greater the amount of adsorbed N2 in all the isotherms of the activated carbon, at activated carbon prepared at 600°C is classified as type I according to the Brunauer, Deming, and Deming-Teller classification.

SEM: (Fig.3) displays electron microscope images of the obtained activated carbons. The external surfaces exhibit significant voids and possess a highly irregular structure, suggesting that the material's porosity resulted from the vigorous action of the activating agent (KOH)[28] during the activation process. Activation at 600°C with KOH led to the formation of a higher number of pores and substantial removal of volatile components [29].Notably, the activated carbon surface displayed large and well-developed pores. The development of pores during pyrolysis played a critical role, enhancing the surface area and pore volume of the activated carbon by facilitating the diffusion of KOHmolecules into the pores.

3.2. Adsorption of MB

3.2.1. Effect of Amount of adsorbent

The effect of adsorbent quantity on methylene blue removal was investigated. For all experiments, the initial concentration of the methylene blue solution was kept constant at 20 mg/L, the initial volume was 50 ml .mass of carbon varied as follows(0.1g,0.2g,0.3g,0.4g,0.5g and 0.6g) The results depicted in (Fig.4) show that removal efficiency increased sharply with increasing activated carbon quantity up to 0.5g. Thereafter, removal efficiencies did not change significantly with increasing adsorbent quantity[30].

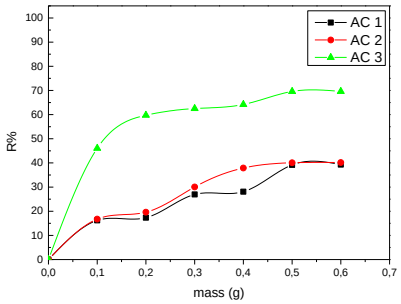

Fig. 4. Effect of adsorbent amount on the removal of methylene blue by adsorption

3.2.2. Effect of initial dye concentration

The efficiency of removal is closely tied to the initial concentration of the adsorbate solution. In order to evaluate the impact of the initial concentration, Amount of adsorbent is 0.5 g,we subjected 50 ml of solutions with varying initial concentrations to the adsorbent. The initial concentrations ranged from 5 mg/L to 20 mg/L, and you can observe the outcomes in (Fig.5).

The graph illustrates a decline in removal efficiency as the initial adsorbate concentrations increase. The total accumulation of methylene blue rises with higher initial concentrations, likely a result of increased interaction between the adsorbent sites and methylene blue. At lower concentrations, the majority of methylene blue in the sample solution can access the active sites of the adsorbent. However, as the concentration increases, not all methylene blue species can effectively engage the active surface because the active sites are already occupied[31].

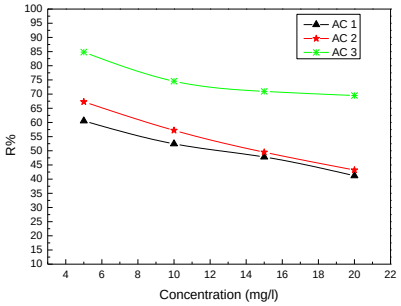

Fig. 5. Effect of initial concentration on the removal of methylene blue by adsorption

4. Conclusions

Activated carbon derived from Juniperusberriesproved to be highly effective as an adsorbent in removing methylene blue from aqueous solutions with remarkable efficiency. Equilibrium adsorption, demonstrating a monolayer of dye molecules adsorbed on the external surface of the Juniperusberriescarbon, was achieved in under 4 hours. The specific surface area (S_{BET}) of the activated carbon was measured at 145.8329 m^2/g,

underscoring its suitability for methylene blue dye adsorption. These findings strongly support the feasibility of utilizingJuniperus berries activated carbon prepared at 600°C as a cost-efficient alternative to commercial activated carbon for the elimination of methylene blue dye from wastewate.

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