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Adsorption of methylene blue from aqueous solutions by activated carbon prepared from hazelnut husk using zinc chloride

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ABSTRACT

In this study, activated carbon prepared from hazelnut husk (HHAC) using zinc chloride as chemical activating agent was characterized by FT-IR spectroscopy, BET surface area, Boehm titration, SEM and elemental analyses. During adsorption from aqueous solution of methylene blue (MB) studied by the batch method, effects of many variables, including solution pH, agitation time, temperature and initial concentration were investigated. It was established that MB adsorption reached equilibrium at 120 min at pH 7.0 as the appropriate value and is more compatible with Langmuir adsorption isotherm with respect to Freundlich. MB adsorption capacity of HHAC was found to be 476.2 mg g^{-1} and MB adsorption kinetics corresponds well with pseudo second order model. Thermodynamic studies revealed that MB adsorption is a spontaneous and endothermic process.

1. Introduction

Coloring agents are widely used to color products manufactured in many industries such as textile, paint, paper, printing [1]. Large amounts of complex dye waste waters are generated as a result of use of too much water during coloring processes, particularly in textile industry. Due to toxic and carcinogenic effects of dyes on living creatures and negative effects to photosynthetic activities of aquatic plants, removal of coloring agents in wastewaters appears to be very important for human health and environment [2,3]. The dyes can be classified as natural and synthetic which are complex organic molecules having groups such as azo, carbonyl, methine, nitro, quinoid, etc. [4]. Methylene blue dye ($C_{16}H_{18}N_3SCl$) is accepted as a model compound for the adsorption of medium size organic molecules [5].

Conventional treatment methods such as biological and coagulation/flocculation are generally unsuccessful for the removal of wastewater containing dyes [3]. An adsorption method is one of the most effective techniques for treatment because of its simple design and low cost [6]. Activated carbon (AC) is one of the most important general purpose adsorbents in the adsorption technique because of its high adsorption capacity, large surface area and high surface reactivity [7]. However, AC is costly, which increases treatment costs. Therefore, recent studies have been focused on the production of low cost AC from various plant-based waste materials such as sugar beet molasses [5], rice husk [8], hazelnut husk [9] and apricot stone [10], and the prepared ACs have been used for the removal of various metal ions or coloring agents from aqueous solutions.

Hazelnut husk (HH) is an agricultural waste that is generated during hazelnut production, not used for any purpose and generally disposed of by burning in open air in threshing area. Since HH is obtained in large amounts (around 140×10^3 tons per annum in Turkey) and has no economic value, it is thought to be an appropriate source for AC production [11]. Previously, some researchers have attempted the preparation of AC from HH and investigated their adsorption abilities [9,11–14]. ACs prepared using phosphoric acid was tested for both removals of metal ion [11] as well as MB [9]. Adsorption ability of AC prepared from HH using $ZnCl_2$ was investigated only for some metal ions [11]. There is no report in the literature about MB adsorption on AC prepared from HH by $ZnCl_2$ activation.

In this study, our objective was to study removal of MB coloring agent from aqueous solutions by AC prepared from HH with $ZnCl_2$. The hazelnut husk activated carbon (HHAC) was characterized by various methods, including FTIR spectroscopy, BET surface area and elemental analysis. During adsorption studies of methylene blue (MB) performed by the batch method, effects of many variables, including solution pH, agitation time, HHAC dosage, temperature and initial concentration were investigated. Adsorption data was

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applied to Langmuir and Freundlich adsorption models, in addition to investigation of adsorption kinetics and thermodynamics of methylene blue adsorption by AC prepared from hazelnut husk.

2. Material and method

2.1. Instruments and chemicals

Shimadzu brand UV-2401 model UV–vis spectrophotometer (Shimadzu, Kyoto, Japan) was used to determine MB concentration in the study. pH measurements were performed by Schott brand CG 840 model pH meter (Schott AG, Mainz, Germany). Adsorption experiments were performed by Nüve ST L02 model waterbath (Nüve A.S., Ankara, Turkey) with an agitator. Nüve brand FN100 model furnace with digital indicator (Nüve A.S., Ankara, Turkey) was used during preparation of HHAC. FTIR spectra of HHAC were recorded using a Shimadzu IR Prestige-21 spectrometer (Shimadzu, Kyoto, Japan) with diamond attenuated total reflectance (ATR) in the region of 4000–600 cm^{-1}.

MB stock solution used in the study was prepared from methylene blue ($C_{16}H_{18}ClN_3S$) with a concentration of 1000 mg L^{-1} purchased from Merck KGaA, Darmstadt, Germany. Working solutions and standard solutions were prepared by diluting from stock solution using distilled-deionized water obtained from Millipore Milli-Q system (Millipore Corp., Billerica, MA, USA). Other chemicals used in the study were analytical grade, unless otherwise indicated, and supplied from Merck KGaA (Darmstadt, Germany). 0.1 M HCl and 0.1 M NaOH solutions were used to adjust pH of MB solutions.

2.2. Preparation and characterization of HHAC

Hazelnut husks were washed with deionized water to remove any dust and debris, followed by drying at 105 °C. Then, it was ground, sieved and a portion with a size of 106–300 μm was used for AC production. 20 g HH and 20 g $ZnCl_2$ were mixed to obtain a ratio of 1:1 by weight. Distilled water enough to wet this mixture (100 mL) was added, mixed well, and allowed to stand for 24 h at room temperature. Then, it was dried at 105 °C for 24 h and carbonized in nitrogen atmosphere at 700 °C. Carbonization process was continued for 4 h and the resultant AC was boiled in 2 M HCl (approximately 200 mL) and filtered off. Treatment of AC with HCl following filtration was performed thrice. Then, AC was rinsed with distilled water until no chloride ion remains in washings. Presence of chloride ion was checked by 0.1 M $AgNO_3$. The obtained HHAC washed was dried at 105 °C for 24 h and used thereafter in this study.

HHAC's ash, humidity, solubility in water, volatile matter content and iodine number determinations were performed according to Standard methods [15]. For pH_{pzc} (point of zero charge pH) determination, after 0.1 g HHAC is mixed with a series of 0.1 M NaCl solutions with an initial pH value in the range of 2–12, resultant suspension was agitated for 24 h. Solution pH was adjusted using 0.1 M NaOH or 0.1 M HNO_3. At the end of agitation, the adsorbent and solution were separated by centrifuging and pH values of the solutions at equilibrium were measured by a pH meter. A plot of ΔpH versus initial pH values was plotted and pH_{pzc} was determined as the value corresponding to the point where the plot intersected x-axis at the value where $y = 0$ [16]. Boehm titration was used to determine lactonic, phenolic and carboxylic groups on the surface of HHAC. In this method, it is possible to distinguish various surface functional groups using NaOH, Na_2CO_3, $NaHCO_3$, where NaOH is considered to neutralize total surface acidic groups (lactonic, phenolic and carboxylic), $NaHCO_3$ lactonic and carboxylic groups and Na_2CO_3 carboxylic groups, hence the quantity of these groups were calculated. For this purpose, 1.0 g of activated carbon is individually agitated with 0.1 N 50 mL NaOH, $NaHCO_3$ and Na_2CO_3 at 400 rpm for 24 h. Then, samples were filtered with vacuum filtration set up and collected in an erlenmeyer. Twenty milliliters of filtrates were titrated with 0.1 N HCl and quantities of the surface functional groups were calculated (mmol g^{-1}) [17–19]. The surface area of HHAC was calculated by applying the BET (Brunauer, Emmett and Teller) equation to N_2 sorption isotherms obtained by NOVA 2200e Quantachrome Autosorb surface analyzer (Quantachrome Instruments, Florida, USA).

2.3. MB adsorption experiments

In order to investigate the effect of agitation period, pH and initial concentration on MB adsorption, 50 mg HHAC was added into 100 mL MB solutions with known concentrations and pH for a predetermined time at 25 °C. Time in the range 2–250 min, pH in the range of 3–12 and initial concentration of MB in the range of 50–800 mg L^{-1} were changed in order to study these factors. To investigate effect of temperature, 50 mg HHAC was added to MB solutions with a concentration of 200 mg L^{-1} with a pH 7.0 and agitated at four different temperatures, (i.e. 25, 35, 45, 55 °C) for 120 min MB concentrations of the solutions obtained at the end of all adsorption studies were measured by a UV–vis spectrophotometer after appropriate dilutions. Each experiment was performed at least in triplicate and the results were presented to be their averages. Concentration of MB that remained unadsorbed in the solution was determined and percentage of adsorption and amount of MB adsorbed per gram of HHAC were calculated by the following formulas, respectively [14],

$$\text{Adsorption}\,\% = \frac{(C_0 - C_e)}{C_0} \times 100$$

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where, q_e is amount of MB adsorbed per gram of HHAC (mg g^{-1}); C_0 is initial MB concentration (mg L^{-1}); C_e is concentration of MB that remained unadsorbed in the solution (mg L^{-1}); V is volume of MB solution (mL); m is amount of HHAC (g).

3. Results and discussion

3.1. Characterization of HHAC

Table 1 shows results of elemental analysis, amounts of surface functional groups, moisture, volatile matter, fixed carbon, solubility in water and ash and iodine number, pH_{pzc}, BET surface area values regarding the AC prepared with $ZnCl_2$ from HH.

Carbon content of HHAC was found high, as expected. C% contents of some ACs were reported to be 64.41–89.71 for ACs prepared from olive pits [20], 70.0–80.1 for ACs produced from sugar beet bagasse [21]. Adsorption properties of ACs depend on surface area and porous structure, as well as on ACs chemical structure to a large extent [22]. It is expected that HHAC could effectively adsorb MB because of its high surface functional group content of the surface. High amount of ash is not desired because it reduces mechanical resistance and adsorption capacity of ACs [23]. Therefore, HHAC's low ash content is important. One of the basic properties of ACs is their high surface area. Surface areas of different ACs reported to be prepared from sawdust of *Tectona grandis* seed by $ZnCl_2$ was 585 m^2 g^{-1} [24], from wild rose seeds by pyrolysis 799.2 m^2 g^{-1} [25], and from pomegranate seeds by $ZnCl_2$ 709.4 m^2 g^{-1} [26]. HHAC has BET surface area higher than most of the ACs prepared from various plant-based materials by $ZnCl_2$ reported in the literature, which suggests that HH is a material that