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Original Research Paper

The synthesis, activation and characterization of charcoal powder for the removal of methylene blue and cadmium from wastewater

Nicoleta Popa [a,b], Maria Visa [b,*]

[a] Department of Forest District Teliu, National Admin. State Forests Romsilva, Romania
[b] Transilvania University of Brasov, Centre of Renewable Energy Systems and Recycling, Eroilor 29, 500036 Brasov, Romania

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ABSTRACT

Charcoal prepared from biomass, wastes of the local forest (tree branches), activated with NaOH solution and with Degussa P25 (TiO_2) was used as adsorbent and photocatalyst for the removal of cadmium cations and methylene blue from wastewater. These materials were characterized by using atomic force microscopy for roughness surface. The energy dispersive X-ray (EDX) spectroscopy and X-ray diffraction (XRD) analysis indicate the existence of nano TiO_2 on the charcoal surface. Additionally, the FT-IR spectroscopy measurements indicate that the alkali treatment develops hydroxyl groups on charcoal surface which could adsorb methylene blue, heavy metals and other pollutants via the synergistic effect. The activities of the charcoal (BC), activated charcoal (BCA) and BCA/TiO_2 mixture (BCA-D) depend on the contact time, adsorbent dosage and pH. The adsorption kinetic data were tested using pseudo-first-order, pseudo-second-order and intraparticle diffusion models. The kinetic studies showed that the adsorption is followed by the pseudo-second-order reaction with regard to the intraparticle diffusion rate kinetics.

1. Introduction

Enhanced industrial activity during recent decades has led to the discharge of volumes of wastewater which is a serious cause of environmental degradation. Many industries, such as textile dyeing and finishing, leather tanning, hair colourings, paper industry, food technology, use the dyes for colouring their products, which involves large amounts of water. It is estimated that more than 100,000 commercially available dyes with over $7 \cdot 10^5$ MT of dye-stuff are produced annually [1] and are used in the textile industry. It is estimated that approximately 15% of dye stuff are discharge in industrial effluents during the manufacturing and processing operations [2].

The residual dye discharge in surface water generates a problem for aquatic life. The wastewaters are loaded with a variety of pollutants such as, dyes, heavy metals and surfactants, and they contain a variety of organic compounds which are harmful and have carcinogenic properties. All synthetic dyes have complex chemical structures with one, two or more aromatic rings with chromophore groups: antrachinone, azo (—N=N—), thiaxine – [3], with heavy metals, i.e. Pb, Cd, Cu, Co, Cr (metal-complex dyes) [3,4], such as their complete biodegradation is slow or even impossible.

Methylene blue (MB) is a cationic dye having various applications: in dyeing industry (dyeing cotton and silk), in chemistry and biology. It is not strongly hazardous but can cause harmful effects: increased heart rate, vomiting, Heinz body formation, cyanosis, jaundice, and tissue necrosis in humans. On inhalation, it can give rise to short periods of rapid or difficult breathing while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, mental confusion and methemoglobinemia [4]. The presence of MB or other dyes in water, even at low concentration, is highly visible, reduces sunlight penetration, and inhibits the growth of aquatic biota [5,6]. Many drugs can interact with methylene blue. A dangerous drug interaction could occur, leading to serious side effects.

The presence of heavy metals in wastewater is unwanted due to their solubility in water. Thus, they can be absorbed by living organisms and they enter in the food chain, start to accumulate in the human body and can cause serious health disorders.

The conventional methods of removing organic/inorganic pollutants from wastewaters are: chemical coagulation [7], electro-flocculation and ozonation [8], biological treatment [8], electrochemical treatment [9], chemical precipitation, chemical oxidation [10], nanofiltration membranes [11,12] and adsorption [13–15]. The adsorption technologies is an effective way for removing dyes, surfactants and heavy metals from industrial effluents, in terms of initial cost, easy operation, simplicity of design,

* Corresponding author. Fax: +40 268 41 05 25.
E-mail address: maria.visa@unitbv.ro (M. Visa).

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inexpensive equipment, less land area (half to quarter of what is required in a biological system) superior removal of organic contaminants [16] and the adsorbents regeneration.

Utilization of the charcoal (potential substitute for activated carbon) [17] activated carbon [18,19] obtained from trees, from bamboo [20,21], wood ash [22] have attracted worldwide attention in view of the large disposal problem with no detriment to the environment. The activated carbon derived from agricultural waste was the most widely used of all the general-purpose industrial adsorbents [23,24]. They are manufactured from a variety of precursors, i.e. cheap and available materials such as wood [25], peat [26], eucalypt bark [27] sawdust [28], rice-husk [29], wheat straw, corncobs and barley husks [30], pine tree leaves [31]. The reactive dye was removed from aqueous solutions by adsorption onto activated carbons prepared from sugarcane bagasse pith [16], etc. which represent carbonaceous precursors for the removal of dyes from water and wastewater. The advantage of using agricultural by-products as raw materials for manufacturing-activated carbon, charcoal, and fuel is that these raw materials are renewable and potentially less expensive to manufacture.

The activated carbon is widely used as a support in water remediation because of its good adsorbance, while the supported TiO_2 exhibits a synergism that has marked effects on the pollutants disappearance kinetics and each pollutant being more rapidly photodegraded [30,31].

To the best of our knowledge, no study has been reported on the preparation of charcoal from tree branches (forest waste) by pyrolysis process, on the basis of intake limited air and measured in specially built to facilities called "Bosha" under limited and controlled air supply.

Therefore, the main objective of this study was to evaluate the possibility of using charcoal (BC) to develop new materials with low cost and its applications for the removal methylene blue and Cd^{2+} cations from aqueous solution by adsorption and photocatalysis.

The adsorbent quality plays a key role and, during the past years, the use of substrates based on modified wastes received plenty of attention because two problems are solved simultaneously: the wastewater treatment and the forest waste use as raw materials. In this way new applications for second range raw material were identified.

2. Materials and the preparation of substrate

Tree branches were collected from deciduous forests (beech, hornbeam) were carbonized with an insufficient amount of air and, then, heated up to temperatures of 400–550 °C through the channel ignition and flue draft. This process was interrupted when the smoke coming through the stack turned bluish. Then, the channel was obturated and is left so few days to cool. The process of obtaining charcoal from wood waste (BC) can be divided into three steps:

1. Drying: in this phase water is eliminated from branches, virtually drying occurs between 0 and 110 °C;
2. Dry distillation: occurs between 150 and 350 °C. At 180 °C hemicelluloses and 1/3 of cellulose usually begins to decomposition, and the wood resistance drops significantly when the temperature reaches 260 °C;
3. Charcoal formation: The beginning of this stage is at 350–400 °C, ending at 400–550 °C, depending on the production conditions. This stage is characterized by removing large amounts of incondensable gases resulting from breakdown of cellulose and lignin [32].

This charcoal and activated charcoal were used for the removal of dye (MB) and heavy metal (Cd^{2+}) from wastewater.

2.1. The activation of BC with NaOH

The raw charcoal was sieved and the 40–100 μm fractions were selected for the experiments. The raw charcoal (BC) shows a limited adsorption affinity for methylene blue and cadmium cations as a result of high surface charge heterogeneity. The next stage of the substrates preparation was washing. Previous studies [33] also proved that an optimum surface charge of the adsorbents is obtained by washing with using NaOH 1N or KOH as modifiers. The washed charcoal (BC) was further mixed with NaOH 1N solution and stirred 48 h at room temperature followed by filtration, rinsing and drying, at 105–120 °C till constant mass. This substrate was noted (BCA).

2.2. The activation of BCA with Degussa P25

To improve the adsorbance and photocatalytic properties of the BCA substrate under UV and VIS radiations, a new substrate noted as BCA-D was developed by adding the TiO_2 (Degussa P25, 80% anatase and 20% rutile) to the BCA substrate in ratio 1:1. The new composite BCA-D, with adsorption and photocatalytic properties for methylene blue and cadmium cations was explored. It is expected that, due to the synergistic effect of the exposed functional groups (—OH) and TiO_2 on the charcoal surface, BCA-D will exhibit a good adsorption and photocatalytic ability in the wastewater treatment process.

3. The materials characterization

The surface morphology of the substrates were observed using Scanning Electron Microscopy (SEM, model S-3400N-Hitachi). The SEM images were obtained at 20–30 kV. The surface elemental composition was evaluated using Energy dispersive X-ray (EDX) measurements. The surface roughness and macro-pores size distribution were evaluated using atomic force microscope (AFM Ntegra Spectra, NT-MDT model BL222RNTE). The images were taken in semi-contact mode with Si-tips (NSG 10, at constant force 0.15 N/m with 10 nm tip radius). The FT-IR spectra of the samples were recorded with Spectrum BX Perkin Elmer BX II 75548, λ = 400–4000 nm. The XRD patterns of the samples were recorded using an X-ray diffractometer (XRD Bruker D8 Discover Diffractometer) operating at 40 kW and 20 mA, 2θ range from 10 to 70°, scanning step 0.02°, scan speed 2 s/step.) The micro-porosity and BET specific surface was carried out by N_2 adsorption at 77 K using an Autosorb-IQ-MP, Quantachrome Instruments.

4. Adsorption and photocatalytic experiments

4.1. Methlene blue dye adsorption studies

The synthesized substrates were used to remove the methylene blue, a cationic dye and Cd^{2+} cations. The MB was chosen in this study because of its known strong adsorption onto solids. The stock-solutions were prepared by dissolving an appropriate quantity of MB, ($C_{16}H_{18}N_3SCl$) (Fluka AG, reagent grade) with (319.85 g/mol) molecular weight, and $CdCl_2$ $2.5H_2O$ (Scharlau Chemie S.A., c < 98%), in ultrapure water (Direct-Q3 Water Purification System). The initial concentration of MB is 0.03125 mMol/L and Cd^{2+} in the concentration range of c_{Cd} = 500–510 mg/L.

Ultrapure water with resistivity of ∼18.23 MΩ cm^{-1} was used throughout the whole experiment.