



Photocatalytic activity of transition metal ions-loaded activated carbon: Degradation of crystal violet dye under solar radiation



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ABSTRACT

In this work, activated carbon (AC) was prepared from date palm stone by chemical activation method. Its properties were investigated, the surface of the AC was found to be acidic (pH_{pzc} of 3.95), Brunauer-Emmet-Teller (BET) surface area of $12.7 \text{ m}^2/\text{g}$, with meso and microporous structures. The prepared AC was loaded with Zn(II), Cd(II), Cu(II), and Pb(II) metal ions by adsorption and ion exchange. Scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR) were used to elucidate the morphology, composition, and bonding of loaded metal ions to the functional group on carbon surface. The prepared AC and its loaded metal ions showed significant catalytic activity for the degradation of crystal violet (CV) under solar radiation. The highest photocatalytic degradation rate was obtained using Zn(II)-loaded AC with 80% mineralization in 40 h. The Zn(II)-loaded AC was used for many cycles of photocatalytic degradation of CV without loss in its catalytic efficiency. The highest degradation rate was obtained at pH 6.5. The degradation rate was found to be inversely proportional to the CV concentration and mesh size of the catalyst. The degradation of the CV was found to take place via OH attack.

1. Introduction

Treatment of waste water generated from different industrial activities is essential for environmental protection, especially in Arab Gulf Commonwealth Countries (GCC) because of the large industrial activities and arid areas. After treatment, this water can be used for many activities such as plant irrigation. Chemical and biological methods were used for removal of inorganic pollutant (such as heavy metals) and organic pollutant (such as dyes, pesticides and phenolic compounds) from waste water [1]. These methods include electrocoagulation, membrane filtration, reverse osmosis, chemical precipitation, adsorption, decantation, flocculation, photocatalytic degradation, and biological degradation using bacteria [2–6].

Activated carbon was used as an adsorbent for water purification from organic and inorganic pollutant [7]. Although, it is commercially available, it can be economically prepared from low cost resources such as agricultural waste. In our previous work [8,9], we prepared activated carbon from date palm leaflets and stones that was used for removal of heavy metals and cationic dyes. The main drawback of the adsorption processes using activated carbon is the generation of secondary waste

(i.e. carbon loaded with heavy metals) that should be regenerated or discarded properly. The regeneration of activated carbon can be carried out physically by heating or chemically using different solvent. However, thermal regeneration of loaded activated carbon leads to loss of large quantity of carbon and cannot be carried out in situ. Also, the loss of carbon by heating is catalyzed by the presence of the heavy metals. In addition, chemical regeneration leads to a decrease in carbon porosity, thus, it decreases its physical efficiency [10,11].

Few systematic studies for the application of semiconductor-free activated carbon and activated carbon impregnated with heavy metal for catalytic decomposition of dyes have been reported [12–15]. A recent study have shown the semiconducting properties of activated carbon with energy band gap in the range (3.0–3.6 eV), thus, it was used for photocatalytic degradation of diatrizoate from aqueous solution under UV radiation [12]. Additionally, the absorption of visible light by semiconductor-free activated carbon [13] and production of hydroxyl radical $\cdot\text{HO}$ and superoxide anions $\cdot\text{O}_2^-$ radical in aqueous solution was elucidated by electron spin resonance (ESR) studies [14]. Therefore, semiconductor-free activated carbon was applied for photo-degradation of phenol under visible radiation [15]. Activated carbon

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was also used as a supporting material to enhance the properties of a semiconducting materials such as titanium dioxide and zinc oxide in photocatalytic degradation of organic pollutant from water using visible or UV radiation [16,17].

CV is one of the most widely used organic dye in textile, paper, leather, cosmetic and food industries [18,19]. In addition, it is used as an antimicrobial agent and staining agent for bacteriological and histopathological application. CV was removed from waste water by many techniques such as: electrochemical degradation [20–23], degradation by Fenton or Fenton-like systems [24], and catalytic ozonation using Fe/activated carbon catalyst [25]. Furthermore, it could be removed from waste water through photocatalytic degradation by UV irradiation using hydrogen peroxide and Fenton reagent [26], titania dispersions [27], and silver ion doped titanium dioxide [28].

The main aim of the present study was to investigate the utility of activated carbon prepared from agricultural waste (date palm stones) along with its heavy metal ions-loaded form (secondary waste) as potential catalysts for the photocatalytic degradation of organic dyes. In order to avoid the tedious, high cost procedure and other drawbacks of the regeneration secondary waste, to purify water from organic pollutants without using any additional semiconductor. Among four heavy metal ions examined (namely, Cu (II), Cd(II), Pb(II) and Zn(II)), Zn(II)-loaded AC has shown the most efficient photocatalytic degradation of CV. Moreover, the mechanism of photocatalytic degradation of CV was investigated using methanol, ammonium oxalate, *p*-benzoquinone as scavengers for $\cdot\text{OH}$, hole (h^+), and $\cdot\text{O}_2^-$, respectively.

2. Experimental

2.1. Materials

Activated carbon was prepared from date palm stone. Zn (NO_3)₂·6H₂O; Cd(NO_3)₂·4H₂O, Cu(NO_3)₂·9H₂O, Pb(NO_3)₂·6H₂O, and CV were from Sigma-Aldrich. H₃PO₄ was from Merck.

2.2. Preparation of activated carbon

Date palm stone was collected, washed with deionized water, dried at 80 °C for 4 h, and crushed. The crushed sample (100 g) was soaked in 250 mL of 10 M H₃PO₄ for 24 h at room temperature, then, carefully washed several with deionized water and heated at 250 °C for 24 h in ambient atmosphere. The produced carbon was washed with 1% NaHCO₃ until the pH of the washings becomes 6, dried in an oven at 100 °C for 5 h, ground using a mortar and pestle, and sieved into different mesh size.

2.3. Loading activated carbon with heavy metals

Heavy metal ions were loaded on the surface of activated carbon through ion exchange with carboxylic acid hydrogens and other acidic sites and complexation with function groups on the surface besides their physical adsorption. These metals exchange with hydrogen of carboxylic group and form complexes with other acidic function groups on activated carbon surface beside their physical adsorption. A 5 g of AC was added to 500 mL of 1000 mg L⁻¹ of Cd(II), Zn(II), Cu(II), and Pb (II) solutions separately, and was shaken for 24 h at room temperature. The produced carbon was filtered off, washed several times with deionized water and heated in a Muffle furnace (Carbolite) at 250 °C for 4 h. The samples were then stored in plastic containers and kept for characterization and photocatalytic studies. The activated carbon samples were named as AC (for pure activated carbon) and AC_{Zn}, AC_{Pb}, AC_{Cd} and AC_{Cu} for Zn, Pb, Cd, and Cu-loaded AC, respectively.

To determine the quantity of metal ions loaded on the surface of the activated carbon, the concentration of the metal ion was measured before and after equilibrium in the soaking solution by inductively coupled plasma spectroscopy (ICP) using an ICP-OES Varian 710

system. Additionally, it is measured on the surface of AC after loading by ashing followed by dissolution in HNO₃. A 0.5 g of activated carbon (pure or loaded with metal ion) was ashed in a muffle furnace at 650 °C for 12 h, the produced ash was dissolved in 6 M HNO₃, and then analyzed for metal ions by ICP.

2.4. Characterization of activated carbon

The acidic and basic functional groups on activated carbon surface were determined according to Bohame's titration [29]. Iodine and methylene blue numbers were determined as described in ref. [30]. Pure and loaded-on activated carbon were characterized by Fourier transform infrared spectroscopy (FTIR) measurements using a Thermo Nicolet Nexus 870-FTIR spectrophotometer in the range of 400–4000 cm⁻¹. The surface area for the prepared activated carbon was measured by the nitrogen physisorption technique using an Autosorb-iQ system (Quantachrome Instruments). The surface morphology and composition of the activated carbon were characterized using a JEOLJSM-5600 scanning electron microscope (SEM) coupled with energy dispersive X-ray spectrometer (EDX). The chemical states of elements on activated carbon surface were investigated using X-ray photoelectron spectroscopy (XPS) using an ESCALAB-250 system with AL-K_α X-ray. An ion chromatograph (IC) (Dionex IC-90 supplied with an AS-14A column and a conductivity detector) was used to measure the amount of anions that leached from activated carbon and from dye degradation at the end of photocatalytic degradation experiments. pH at the point of zero charge pH_{pzc} of activated carbon was measured using a Zeta sizer (Malvern Instruments, UK).

2.5. Photocatalytic experiments

Photocatalytic experiments were carried out at the UAEU campus under solar radiation during the sunny days of May 2015. The average solar light intensity and temperature at that time and location were 7.8 kWh/sq.m and 39 °C, respectively. A 1.0 g of each sample (AC, AC_{Zn}, AC_{Pb}, AC_{Cd} and AC_{Cu}) was mixed with 250 mL of 100 mg L⁻¹ CV dye in five glass containers. Adsorption properties were measured in dark before the photocatalytic experiment. The results showed that the adsorption equilibrium is attained after shaking in dark for 2 h and 3 h for AC and loaded-on AC, respectively. So, the containers were kept closed in dark under continuous shaking for 20 h before placing them under sun light. Samples were then collected at different time interval. All measurements were performed in duplicate and was expressed as the average of two values. A 250 mL of 100 ppm dye without carbon was placed in another container and placed under sun light. Determination of CV concentration as a function of time was carried out using a UV-vis spectrophotometer (Cary 50, Varian). Before measurement, samples were centrifuged to separate any solid particles from the catalyst.

2.5.1. Effect of scavenger on photocatalytic degradation

The effect of scavenger on photocatalytic degradation of crystal violet was studied using three scavengers. Methanol was used as a scavenger for hydroxyl radical $\cdot\text{OH}$ [31], ammonium oxalate for hole radicals h^+ [32], and *p*-benzoquinone for oxygen radicals $\cdot\text{O}_2$ [33]. A 2 mL of methanol, 10 mg of ammonium oxalate, and 10 mg of *p*-benzoquinone were mixed separately with 50 mL of 25 ppm CV and 100 mg of AC_{Zn} in glass containers. The mesh size of the activated carbon catalyst was 300 μm and pH of the dye solution was 6.5. Samples were left in dark for 20 h before starting the photocatalytic experiments under sun light. To evaluate the effect of different scavengers, samples were collected at different time intervals and were analyzed for CV concentration.

2.5.2. Effect of pH on photocatalytic degradation rate

The effect of pH on photocatalytic degradation rate was studied for

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