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# Adsorptive and photocatalytic removal of reactive dyes by silver nanoparticle-colemanite ore waste

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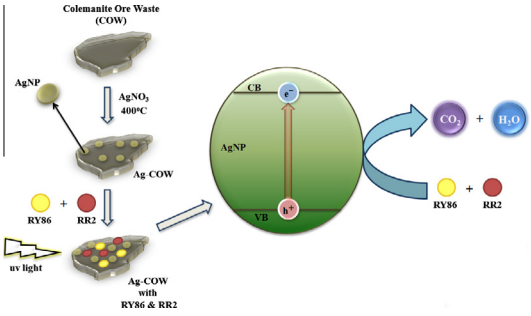
## HIGHLIGHTS

- AgNPs were synthesized using COW without using a chemical reducing agent.
- Ag-COW presented high adsorption of reactive dyes from aqueous solutions.
- Ag-COW exhibited photocatalytic activity for the removal of the reactive dyes.
- Ag-COW presented better photocatalytic performance than $TiO_2$-based systems.

## GRAPHICAL ABSTRACT

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## ABSTRACT

A novel composite containing silver nanoparticles (AgNPs) and colemanite ore waste (COW) was synthesized and tested in adsorption and photocatalysis to remove Reactive Yellow 86 (RY86) and Reactive Red 2 (RR2) from aqueous solution in single and binary dye systems. Transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and X-ray diffraction patterns (XRD) showed the formation of metal AgNPs on COW. The BET surface area increased after intercalation of AgNPs onto COW. Ag-COW was found to be a good material for dye adsorption. The effects of operating variables such as initial dye concentration, pH and contact time in adsorption were studied. The kinetics, isotherm and thermodynamic parameters for the adsorptive removal of the reactive dyes were also investigated. In addition, Ag-COW also shows high photocatalytic activity for degradation of the reactive dyes from single and binary dye solutions. The combination of adsorption and photocatalysis using Ag-COW is demonstrated as a more effective technique for contaminant removal from aqueous solution.



## 1. Introduction

The contamination of water has been a serious problem in last decades [1]. Water pollution is due to the presence of organic and inorganic pollutants from various industries such as textile, plastics, cosmetics, and food. Removal of textile dyes, for example, from wastewater sources is important in water purification process. Recently, several techniques have been performed for the removal of textile dyes from wastewater, including chemical oxidation [2], anaerobic treatment [3], adsorption [4], biosorption [5], coagulation [6], membrane filtration [7] and photocatalysis [8]. Adsorption has several advantages such as high removal efficiency, simplicity and easy operation of textile dyes containing wastewater [9]. A number of researchers have investigated different low-cost adsorbents such as boron waste [10], clays [11], bagasse pith [12], fly ash [13], bottom ash [14], fertilizer waste [15], blast furnaces lag [16], silkworm pupa [17], red mud [18], hen feathers [19] and agricultural waste residues [20]. Many

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research groups also showed $TiO_2$ as a conventional photocatalyst for the effective degradation of dyes [21]. In dye photocatalysis, it can make use of the solar energy in a visible range [22]. During the process, electrons can be stimulated from a photocatalyst for adsorbed dye decomposition. The major advantage of this process is that, compared to other advanced technologies, photocatalysts are self-regenerated and are recyclable or reusable. An ideal photocatalyst should be highly photoactive, stable and non-toxic and meet primary criteria for a higher $H_2O/OH$ couple ($OH^- \rightarrow {\cdot}OH + e^-$, $E^0 = -2.8$ V) [23]. There are many preferred photocatalysts, such as $TiO_2$, $WO_3$, ZnS, and ZnO [22]. The new photocatalysts are still necessary to improve the energy and environmental technologies related with solar energy. Apart from metal oxides, AgNPs show efficient plasmon resonance and enhanced photocatalytic activity in the visible light region. AgNPs are well known to improve remarkable photocatalytic activity by the reduction of electro/hole recombination reaction due to shape-dependent optical properties, its localized surface plasmon resonance and the collective oscillations of their conduction band electrons [24].

The boron ores are important natural resources in Turkey. During boron enrichment process, a large amount of colemanite ore waste (COW) is discharged into waste dams from the boron plants. The waste dams containing boron minerals can cause a big environmental problem [25]. Colemanite ore waste contains colemanite, ulexite, zeolite, calcite and some clays. Colemanite is a boron mineral most found in Turkey with a basic formula "$CaB_3O_4(OH)_3{\cdot}H_2O$" and it contains lots of $BO_2(OH)$ and $BO_3(OH)$ [26]. Previously, it has been demonstrated in many applications as a boron waste [27].

Using industrial solid wastes for adsorption or catalyst support has been proposed in recent years for materials recycling and utilization. In this study, synthesis of Ag NPs with COW was performed without a reducing agent and their photocatalytic performance and adsorptive behavior were investigated in the removal of RY86 and RR2 in single and binary dye solutions with or without UV–vis irradiation. The results show that combination of adsorption and photocatalysis on Ag-COW is quite efficient technique for dye removal.

## 2. Materials and methods

### 2.1. Apparatus and reagents

COW used for support and reduction of silver (I) ions was obtained from Etibor (Emet-Kütahya, Turkey). The chemical composition of COW and Ag-COW was determined by inductively coupled plasma spectrophotometer (Perkin-Elmer Optima 4300 DW ICP-OES). The absorption spectra of dye solutions were determined by a Shimadzu UV/Visible spectrophotometer (UV2550, Japan). TEM images were obtained on a JEOL 2100 HRTEM instrument (JEOL Ltd., Tokyo, Japan). XPS measurements were performed on a PHI 5000 Versa Probe (Φ ULVAC-PHI, Inc., Japan/USA) model X-ray photoelectron spectrometer. The pressure was $10^{-7}$ Pa. X-ray diffraction (XRD) measurement of Ag-COW was performed with a Rikagu Miniflex X-ray diffractometer using mono-chromatic Cu Kα radiation. The BET surface areas of COW and Ag-COW were measured by $N_2$ adsorption–desorption (Quantachrome Corporation, NOVA-2000, USA). A diffuse reflectance spectrum (DRS) of Ag-COW was monitored on a UV-2550 Shimadzu UV–vis spectrophotometer equipped with ISR-2200 DRS accessory.

All other chemicals used in the investigation were reagent grade and included the following: silver nitrate ($AgNO_3$) (Merck), RY86 (MW = 596.01 g mol$^{-1}$, Sigma–Aldrich) and RR2 (MW = 615.34 g mol$^{-1}$, Sigma–Aldrich), ethanol (Merck). The aqueous solutions were prepared using ultra-pure quality of water with a resistance of 18.3 MΩ cm.

### 2.2. Preparation of Ag-COW photocatalyst

The COW was firstly dried at 90 °C for 48 h. Approximately 5 g of COW were added to 500 mL of ultra-pure water under stirring for 1 h. Then 50 mL of 0.1 M $AgNO_3$ solution was also prepared with ultra-pure water. The $AgNO_3$ solution was added to COW solution and allowed for vigorous stirring for 2 h. The mixture solution was centrifuged, washed with ultra-pure water, dried in vacuum and the solid sample was calcined at 400 °C for 4 h under nitrogen atmosphere. The silver content of Ag-COW was determined to be approximately 13.5 wt%.

### 2.3. Batch studies for adsorption

Stock dye solutions at concentration of 1000 mg L$^{-1}$ were prepared and they were diluted to obtain the experimental solutions. Batch experiments were performed in 50 mL flasks at 25 °C in an isothermal shaker with a mixing speed of 200 rpm. For single dye adsorption, the pH experiments were studied by shaking for 60 min at 25 °C, with 50 mg of Ag-COW in 50 mL of dye solution at different pHs. The solution pH was adjusted between 2.0 and 9.0 using 0.1 M HCl or NaOH and measured by a pH meter (Metler Toledo MA 235). Isothermal and kinetic studies were performed at 25 °C. In each run, 50 mg of Ag-COW was in contact with 50 mL of dye solution (25–200 mg L$^{-1}$) at different time intervals (10–110 min) at pH 2.0. The concentration of dye solution was analyzed using a UV–Vis spectrophotometer at certain time intervals. The wavelength values for maximum absorbance ($\lambda_{max}$) of RY86 and RR2 were observed at 416 and 534 nm, respectively. The concentrations of dye solution were calculated using the linear regression equations.

The batch experiments of binary dye solution were performed with a similar procedure. In a binary system with components *A* and *B*, the measurement would be carried out at their maximum absorbance wavelength $\lambda_{max1}$ and $\lambda_{max2}$, respectively, giving absorbances of $A_1$ and $A_2$. Concentrations of dye solution were then estimated quantitatively using the linear regression equations obtained by plotting a calibration curve for each dye over a wide range of concentrations. In a binary dye solution, the concentrations of RY86 and RR2 were calculated according to our previous study [28]. In a binary system with components *A* and *B*, dye concentrations were calculated by the following equations [28]:

$$C_A = \frac{k_{B_2}A_1 - k_{B_1}A_2}{k_{A_1}k_{B_2} - k_{A_2}k_{B_1}} \quad (1)$$

$$C_B = \frac{k_{A_1}A_2 - k_{A_2}A_1}{k_{A_1}k_{B_2} - k_{A_2}k_{B_1}} \quad (2)$$

where $k_{A_1}$, $k_{B_1}$, $k_{A_2}$, and $k_{B_2}$ are the calibration constants for components *A* and *B* at wavelengths $\lambda_{max1}$ and $\lambda_{max2}$, respectively giving absorbances of $A_1$ and $A_2$. $k_{A_1}$, $k_{B_1}$, $k_{A_2}$, and $k_{B_2}$ for components *A* and *B* were obtained using the linear regression equations according to the calibration curve. For binary dye solutions, initial dye concentrations were maintained at 1:1 (w/w).

### 2.4. Photocatalytic oxidation of dyes

Photocatalytic degradation of dyes was performed in a thermo static batch with a UV–vis lamp (400 W, $\lambda$ = 250–570 nm) and quartz glass. The nitrogen gas was passed during degradation of the dyes. The photodegradation experiments of single and binary