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Reutilization of the Cr ions adsorbed on activated carbon as colorants in glass preparation

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ABSTRACT

Microporous activated carbon (AC) was used to absorb Cr(VI) ions in aqueous solutions. To avoid the secondary pollution which might be caused by the spent absorbent, the AC which had absorbed Cr(VI) was applied as colorants in preparing Na_2O–CaO–SiO_2 glasses. XPS analysis results indicate that Cr(VI) ions are partially reduced to Cr(III) ions during the adsorption. It is demonstrated that the adsorbed Cr ions in AC are effective for glass colorization. The color of the glasses varies from dark brown to light green depending on the dosage of the spent AC. In addition, with the same concentrations of Cr ions in glass batches, the color of the resultant glasses significantly depends on the amounts of AC included rather than the valence of the Cr ions, suggesting the above color variations are mainly due to the presence of the AC.

1. Introduction

Toxic heavy metal ions (including chromium, nickel, copper, zinc, mercury, cadmium and lead) in wastewaters have long been concerned. Even at low concentrations, these metal ions are extremely toxic. They have serious impacts on not only environment but also human beings. Fox example, the metal ions can accumulate in food chain through crop irrigation and contaminated drinking water and finally threaten the health of people [1].

Cr(VI)-containing compounds are used in leather tanning, electroplating, metal finishing and many other chemical industries [2], generating Cr(VI)-contaminated waste waters. Owing to its carcinogenicity, Cr(VI) has caused many serious environmental problems. According to the regulations of the United States Environmental Protection Agency, the highest level of total Cr allowed in a drinking water is 0.1 mg/L [3].

Cr(VI) in wastewaters could be removed by chemical precipitation,ion exchange, electrochemical precipitation, chemical reduction,solvent extraction, membrane separation, reverse osmosis and adsorption/biosorption, etc. [4]. Among these methods, the adsorption of the ions with absorbents is considered as a simple, relatively low-cost and effective method. Various absorbents such as zeolite [5], hydroxyl apatite [6], functionalized silica [7], peanut hulls [8], polypyrrole/maghemite nanocomposite [9], modified chitosan [10–12] and activated carbon (AC) [13,14] have been studied.

AC is a conventional porous absorbent with a large surface area, high porosity and variable pore size distribution [15]. It has attracted great attention in wastewater treatment due to its low cost, abundance and high efficiency. In addition, AC absorbent itself is an environmentally friendly material [16]. Many studies have focused on improving the efficiency of AC toward the heavy metal ions in wastewaters. For example, Wang et al. [17] improved the removal efficiency of Cr(VI) by quaternary amine modification of the AC, resulting in an adsorption capacity of 112.36 mg/g. Liu et al. [13] modified the AC from Zizania caduciflora with tartaric acid during its phosphoric acid activation process. Due to the inclusion of oxygen-containing functional groups, more electrons were provided for the Cr(VI) reduction to Cr(III) and consequently a high removal efficiency had been achieved. However, to our knowledge, much less concern has been given to the spent AC. The used absorbents which have absorbed Cr contaminants will become secondary pollutants.

We note that transition metal ions are used in the preparation of color glasses. The excitation of the 3d or 4f valence electrons of the transition metal ions in glasses may cause selective absorptions of the visible light, leading to the colorization of the glasses. The spectral characteristics and the color of the glasses mainly depend on the electric field strength, valence and oxygen coordination number of the ions. Other factors including glass composition,

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Table 1
Colorant dosage and the charging temperature of the glass batches.

Glass sample	Charging temperature (°C)	Colorant	Colorant in batch (g)	Metal ions in batch (mg/g)
G-Cr-1	1200	AC-Cr-10	4.24	0.479
G-Cr-2	1200	AC-Cr-10	2.16	0.244
G-Cr-3	1200	AC-Cr-10	1.43	0.161
G-Cr-4	1200	AC-Cr-10	0.672	0.076
G-Cr-4′	Room temperature	AC-Cr-10	0.712	0.078
G-Cr-5	1200	AC-Cr-50	1.608	0.479

melting temperature, time and atmosphere also have influence on the ion colorization. Typically, Cr(VI) gives a silicate glass a yellowish color, while Cr(III) gives a green color and is widely used in the production of glass bottles for beers.

In this work, an AC was used to absorb Cr(VI) from aqueous solutions. After the absorption, the residue of the spent AC containing the adsorbed ions was applied in the preparation of Na_2O–CaO–SiO_2 glasses. The transmission spectra of the obtained glasses were recorded. The influence of the AC absorbent on the glass coloration is discussed.

2. Experimental

2.1. The adsorption of Cr(VI) by the AC

A Cr(VI) solution with a concentration of 10 mg/L was prepared by dissolving analytic grade $K_2Cr_2O_7$ (Tianjin Guangcheng Chemical Reagent Company) in distilled water. 0.2 g of the AC power (Laiyang Fine Chemical Factory, China) was added into 100 mL of the chromium solution. The pH of the solution was adjusted by diluted H_2SO_4 (49%) to 2 [13,18]. The mixture was shaken in an incubator at 25 °C for 1 h. After the adsorption process, the absorbent was filtered out and dried at 90 °C. The sample was named as AC-Cr-10.

For comparison, the initial Cr(VI) concentration was increased to 50 mg/L. All procedures were the same as the above mentioned except that the adsorption time was extended to 3 h. The sample was encoded as AC-Cr-50.

2.2. The preparation of the color glasses

Glasses with a composition of Na_2O 22%, CaO 12%, SiO_2 60%, MgO 4%, Al_2O_3 2% by weight were prepared to verify the effect of the colorants. Analytic grade of silica, sodium carbonate,

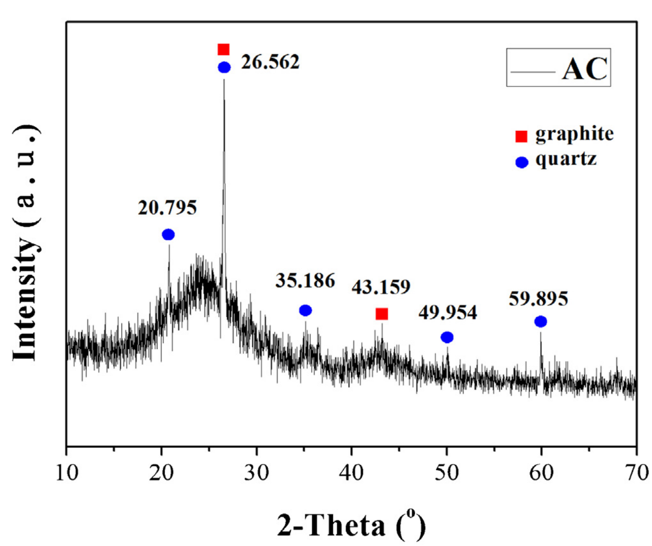

Fig. 1. The XRD pattern of the activated carbon.

aluminum hydroxide, calcium carbonate and magnesia were used as reagents for preparing glass batches. Sb_2O_3, $NaNO_3$ were added as clarifying agents and CaF_2 as a fluxing agent. AC-Cr-10 and AC-Cr-50 were respectively added into the batches as the colorants. Reducing amounts of AC-Cr-10 were applied and the resultant glass samples were labeled as G-Cr-1, G-Cr-2, G-Cr-3 and G-Cr-4, respectively. The glass samples prepared with the addition of AC-Cr-50 was encoded as G-Cr-5.

The raw materials were proportionally weighted and thoroughly mixed. The batches were added into crucibles which were preheated to 1200 °C and further melted in an electric furnace at 1350 °C for 2 h. The glass melts were then casted in a steel mould. The formed glasses were annealed at 500 °C for 2 h.

Compared with sample G-Cr-4, the same batch which contained the AC-Cr-10 was put into a crucible and heated from room temperature to the melting temperature. The corresponding sample was designated as G-Cr-4′.

The detailed information of the colorants and the glass batches can be found in Table 1.

2.3. Characterization methods

The X-ray diffraction (XRD) pattern of the AC was recorded on D8 Advanced diffractometer (Bruke, Germany). The scanning electron microscopy (SEM) analysis on the AC was performed on a QUANTA-250-FEG (FEI, USA) microscope. The particle size distribution of the AC was measured on an LS13320 laser particle size analyzer (Beckman, USA). The powder was dispersed in ethanol under ultrasonic vibration. N_2-sorption measurement of the AC was performed on an ASIQC0000-4 automatic gas adsorption instrument (Quantachrome, USA). The surface area was calculated using the multi-point BET method. The pore volume was determined using the data at the relative pressure close to 1 and the pores size was evaluated by the HK method [18].

The concentrations of the Cr(VI) in the solutions were determined according to the standard of 1.5 Diphenylcarbohydrazide spectrophotometric method on a 722 visible light spectrometer (Jinghua, China). The valence of the chromium ions in the AC was analyzed by the X-ray photoelectron spectroscopic (XPS) technique on a Thermo esca lab 250 Xi spectrometer (Thermo Electron Corporation, USA).

The transmission spectra of the prepared glasses were recorded on a 722 visible light spectrometer (Shanghai, China). The glass samples were cut and polished. The samples for the optical spectra measurements were about 5 mm thick.

3. Results and discussion

3.1. The specification of the AC powder

The XRD pattern of the AC is depicted in Fig. 1. From this pattern, the broad diffraction peaks characteristic of amorphous carbon are visualized at 2θ degrees of 20–30° and 40–45° [19]. However, the peaks at 26.562° and 43.159° can be indexed to the hexagonal graphite phase (JCPDF card, No. 26-1079), indicating that the AC was partly graphitized. In addition, the peaks at 2θ = 20.795°,