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Synthesis of highly effective absorbents with waste quenching blast furnace slag to remove Methyl Orange from aqueous solution

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ABSTRACT

Water quenching blast furnace slag (WQBFS) is widely produced in the blast furnace iron making process. It is mainly composed of CaO, MgO, Al_2O_3, and SiO_2 with low contents of other metal elements such as Fe, Mn, Ti, K and Na. In this study, WQBFS was treated with grinding, hydrochloric acid acidification, filtration, filtrate extraction by alkali liquor and a hydration reaction. Then BFS micropowder (BFSMP), BFS acidified solid (BFSAS) and BFS acid-alkali precipitate (BFSAP) were obtained, which were characterized by X-ray diffraction, scanning electron microscopy, X-ray fluorescence and Brunauer-Emmet-Teller (BET) specific surface area. The decoloration efficiency for Methyl Orange (MO) was used to evaluate the adsorptive ability of the three absorbents. The effects of adsorptive reaction conditions (pH and temperature of solution, reaction time, sorbent dosage and initial concentration) on MO removal were also investigated in detail. The results indicated that BFSAP performed better in MO removal than the other two absorbents. When the pH value of MO solutions was in the range 3.0–13.0, the degradation efficiency of a solution with initial MO concentration of 25 mg/L reached 99.97% for a reaction time of 25 min at 25°C. The maximum adsorption capacity of BFSAP for MO was 167 mg/g. Based on optimized experiments, the results conformed with the Langmuir adsorption isotherm and pseudo-second-order kinetics. Among inorganic anions, SO_4^{2-} and PO_4^{3-} had significant inhibitory effects on MO removal in BFSAP treatment due to ion-exchange adsorption.

Introduction

Blast furnace slag (BFS) is a co-product of the iron manufacturing process. According to the control mode used for cooling rate and time, it can be divided into water quenching blast furnace slag (amorphous state) and air cooling blast furnace slag (crystalline state). Whether in the amorphous or crystalline state, the slags have similar chemical components and mainly contain CaO, MgO, Al_2O_3, SiO_2, and other minor components such as Fe_2O_3, MnO_2, K_2O, Na_2O and TiO_2. Since the water

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quenching technology has the advantages of simple operation, lower space requirements, low cost and fast processing time, more than 75% of iron and steel enterprises adopt this technique to treat blast furnace slag in China. In 2014, the global output of pig iron output was 1.179 Gt, with China accounting for more than 60%. According to empirical calculations, the BFS production is approximately 400 kg/ton pig iron. A large amount of BFS not only requires space to store and manage, but also causes serious environmental pollution (water, air and soil). Therefore, comprehensive utilization and recycling of BFS is very crucial for sustainable development of steel enterprises (Yang et al., 2013; Ren et al., 2014; Yan, 2012; Chen and Liu, 2007).

Methyl Orange (MO) is a typical dye and has been widely used in many industrial processes. MO-containing wastewater is toxic and resistant to biodegradation. Thus, many physicochemical methods have been developed to remove MO from aqueous solution. Adsorption processes have many advantages including simple operation, high efficiency, fast reaction and so on. The developed adsorbents for MO removal include synthesized metals/semiconductors, oxide/graphene nanocomposites, metal oxide/nano-size materials, metal oxide/porous materials and porous materials. In photo-catalytic processes, metal oxides have been loaded on the surface of natural or synthetic ores to decompose H_2O_2 to form hydroxyl radicals (Wang et al., 2015; Zheng et al., 2015; Dou et al., 2015; Barbosa et al., 2015). In general, these materials, such as activated carbon, zeolite, rare earth, kaolin, diatomite, et al., exhibit a porous structure and large specific surface area. Adsorption of MO has been studied using layered double hydroxides (LDH), layered double oxides (LDO) and hydrotalcite-like materials in acidic conditions, under certain conditions of reaction time and temperature (Zhang et al., 2014a; Kuwahara et al., 2013; Wang et al., 2015). As-prepared ZnAl-LDHs and LDOs showed excellent adsorption capacity toward MO in aqueous solution (Li et al., 2014). The adsorption behavior and mechanism of reactive brilliant red X-3B in aqueous solution over three kinds of hydrotalcite-like LDHs and found that these hydrotalcite-like LDHs have a relatively high adsorption rate in the pH range of 3–9 (Zhang et al., 2014b). The red dyes (Reactive Red, Congo Red and Acid Red 1) were removed efficiently by Mg–Al-LDH, and showed clearly that the optimal dosage and contact time for Mg–Al-LDH were 0.10 g and 60 min, and that pH had little effect at pH < 10 (Shan et al., 2015).

In this study, our aim was to use waste blast furnace slag to synthesize absorbents to remove MO from aqueous solution. In detail, the waste blast furnace slag was treated and synthesized into three materials (BFS micropowder (BFSMP), BFS acidified solid (BFSAS) and BFS acid-alkali precipitate (BFSAP)). These materials were characterized by X-ray diffraction, BET surface area and scanning electron micrograph. Their adsorptive ability for MO removal was compared according to decoloration effectiveness. In addition, the effect of reaction conditions (pH, temperature, initial MO concentration, inorganic anions) on MO removal was also investigated. This study aimed to provide a feasible solution for synthesizing adsorbents from waste BFS for MO-containing wastewater treatment.

1. Materials and methods

1.1. Sample description

All chemicals used were of analytical grade and supplied by Sinopharm Chemical Reagent Co., Ltd. WQBFS was supplied by the ZhongYang Steel Co., Ltd., China and its chemical composition is given in Table 1. Ultra-pure (UP) water was used throughout the experiments.

1.2. BFS pretreatment

WQBFS was ground by a ball mill to a particle size less than 38 μm to give BFSMP. BFSMP (10.0 g) and hydrochloric acid (200 mL, 3 mol/L) were mixed in a conical flask and covered with sealing film, and kept for 2 hr in a 95°C water bath. The insoluble solid was separated with a filtration membrane and then washed with ultra-pure water, then the solid residuals were dried and collected as BFSAS. Then, the pH of the supernatant was adjusted to 11.0 ± 0.1 using 0.8% sodium hydroxide solution and covered with sealing film, and kept for 18–20 hr in a 60°C water bath. The suspension was centrifuged to separate the sediments, which were dried at −55°C with a freeze–drier and then collected as BFSAP for use (Fig. 1).

1.3. Adsorption experiment with Methyl Orange solution

MO solutions were prepared at concentrations of 0.0 mg/L, 0.5 mg/L, 1.0 mg/L, 1.5 mg/L, 2.0 mg/L, 2.5 mg/L, 4 mg/L and 8 mg/L, respectively. The absorbance of the solutions was determined using a double-beam UV–Vis spectrophotometer to construct a standard curve for MO quantification in the following work.

BFSMP, BFSAS and BFSAP of different doses were placed into the prepared series of MO solutions in 50 mL colorimetric tubes respectively. The tubes were then stirred for 30 min at 25°C in a gas bath thermostatic oscillator at a constant shaking rate. The absorbents were removed with a syringe with filter and the absorbance was measured using a double-beam UV–Vis Spectrophotometer.

Table 1 – Chemical composition of blast furnace slag (BFS) micropowder (BFSMP), BFS acidified solid (BFSAS) and BFS acid-alkali precipitation (BFSAP).

Compound	BFS (Unit status, %)	BFSAS (Unit status, %)	BFSAP (Unit status, %)
SiO_2	32.01	86.79	0.00
Al_2O_3	14.94	0.49	18.30
Fe_2O_3	0.31	0.02	0.34
MgO	9.55	0.33	24.93
CaO	36.11	1.32	11.92
Na_2O	0.23	0.02	14.19
K_2O	0.22	0.02	0.37
MnO	0.46	0.03	0.51
TiO_2	1.15	0.16	1.10
P_2O_5	0.01	0.01	0.01
CO_2	0.00	0.00	15.42
H_2O	5.01	10.81	12.91