Strip-like wet bottom slag-based geopolymer as an adsorbent for removal of heavy metal ions

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Abstract. The strip-like wet bottom slag-based geopolymer mixed with PES-NMP solutions, which used sodium hydroxide and sodium silicate as alkali activators, wet bottom slag as base materials respectively, were prepared by phase transition method. The as-prepared WBS geopolymer powder and strip-like adsorbents were systematically characterized by XRF, BET, XRD, SEM and heavy metal adsorption respectively. The experimental results presented that wet bottom slag had the potential to use as the base materials of geopolymer, which can form the amorphous structure, higher surface area and a bigger pore volume. That makes the adsorption of heavy metal to come true. When the heavy metal amount as 20 mg/L of each Fe²⁺ and Cu²⁺ ions, 40 mg/L of Mn²⁺, the as-prepared WBSG- PES-NMP strips showed the highest absorption capacity of 56.8%, 63.2% and 88.4% respectively.

1. Introduction

Wet bottom slag (WBS) is the byproduct of coal combustion via the slag tapping boiler process, and the amount of its discharge is huge. Taking 300MW set of slag tapping boiler for an example, 2000 t of coal could be consumed per one day; and 200 t of wet bottom slag would be produced. The slag tapping boiler application of China ranks first in the world, therefore, China is also the largest wet bottom slag producer in the world. With the more stringent environmental protection, the utilization of cumulative wet bottom slags in China would cause a major concern in the world. The high content of silica and alumina makes it possible to use the WBS in alkali-activated aluminosilicate material or geopolymer. The geopolymer with three-dimensional reticular structure was first introduced by Davidovits in 1979, which was composed by the materials containing abundant alumina and silica that was activated by using alkaline solution to serve as an alternative or replacement to ordinary Portland cement [1, 2].

Recent studies investigated the use of low cost and eco-friendly inorganic polymers. The properties of geopolymers are largely dependent on the characteristics of the base materials (chemical composition, glassy phase, amount of soluble silicon and aluminum, particle morphology, mineralogical structure, particle size distribution, and presence of inert particles). The excellent base materials should have enough content of spherical glass beads, and possess an exceedingly amorphous
structure, outstanding ability to easily release aluminums, and low water demand [3]. Wet bottom slag can just meet the requirements.

Meanwhile, the study of the use of geopolymers as adsorbents is fairly recent. For adsorption, geopolymers have a negatively charged aluminosilicate network, balanced by cations such as sodium or potassium, which may in turn be exchanged with cations in solution, have high cations exchange capacity and large capture range for cationic heavy metal. The characteristics suggest the feasibility of using inorganic polymers as heavy metal adsorbent materials [4, 5]. The use of powdered adsorbents is the research focus, which cannot be easily recovered, and so cannot be directly used in field applications. Powdered adsorbents are difficult to use as adsorption, because of the use of supporting materials (e.g. porous ceramics, polymer foams), the complicated procedures with a separation step (e.g. pressure filtration) and high temperature. Strip adsorbents produced by the phase transition method are relatively simple, as the cheap investment and room temperature condition [6, 7].

In this paper, geopolymer composition strip was produced and evaluated as heavy metal adsorbents. Based on the former research from other experts, there has little research work studied yet to produce the geopolymer composition strip by phase transition method. The geopolymer composition strip can be easily handled, recycled and application potential for heavy metal wastewater treatment.

2. Experimental procedure
Wet bottom slag (WBS) obtained from a heat and power plant in China with the chemical compositions, as shown in Table 1. The wet bottom slag was dried in a laboratory oven at 105°C for 4 h and grinded by a small ball mill. The particle size distribution (PSD) range of WBS is between 1 μm and 10 μm (D (90) < 85 μm). For the activation, 96% sodium hydroxide and sodium silicate with a modulus of 3.3 (26.5% SiO₂, 8.3% Na₂O, 60% H₂O) were selected as the alkali activators.

| Component (wt%) | SiO₂ | Al₂O₃ | CaO | Fe₂O₃ | K₂O | Na₂O | MgO | TiO₂ | SO₃ |
|-----------------|------|-------|-----|-------|-----|------|-----|------|-----|
| WBS             | 47.47| 14.39 | 17.03| 15.73 | 1.51| 0.89 | 0.74| 1.05 | 0.10|

The mineral components of original wet bottom slag by X-ray diffraction (XRD) and demonstrated the results in Figure 1. Based on smoothing and fitting the XRD of WBS and the analysis of crystallinity of WBS sample by Jade software, it was found that the crystallinity of raw samples is 1.51% and the number in parentheses above means variance. Besides, the amorphous phase includes silicon and aluminum mineral composition.

Figure 1. XRD patterns of WBS in original state.
The geopolymer slurry was synthesised using an approach, in which 60 g of aluminosilicate precursors (100 wt.% WBSG) were mechanically mixed with 28.59 g of alkaline solution, 1.98 g of water and 0.12 g of pore forming agent to produce the geopolymer slurry. Afterwards, wet bottom slag-based geopolymer (WBSG) slurry was poured into a steel mold and cured at 20 °C and 90% relative humidity for 24 hr in a climatic chamber, which promoted the solidification of the slurry. And finally the specimens were cured at room temperature for 27 days in a water chamber, before being used as the geopolymer composite strips. Afterwards, the WBSG sample was ground and sieved through sieve 125μm square-mesh sieve. The geopolymer powder was washed with distilled water until the washed water showed pH at 7.0 ± 0.5 and then dried at 60 °C for 24 hr.

The geopolymer composite strips were fabricated by phase transition of the Polyethersulfone (PES) – N-Methyl-2 pyrrolidone (NMP) solution and extrude to solid in water, which is shown in in Figure 2. For preparing PES-NMP solution, 30 wt% of PES which is polymer was dissolved in NMP solution (solvent). WBSG powder was added to the PES-NMP solution at 50 wt%. Then, the mixed slurry was agitated for 1 day and extruded through a cylindrical mounting gun with a diameter of 0.5 cm and dropped into water bath containing the deionized water at 25 °C. The strip structure is mainly achieved from a combination of phase separation method and mass transfer [8]. The WBSG-PES-NMP strips was washed with distilled water at 80 °C to remove residue NMP solution and dried at 60 °C for 24 hr.

![Figure 2. XRD patterns of WBS in original state.](image)

S4-Explorer (produced by Bruker company, Germany) x-ray fluorescence spectrometer (XRF) was introduced to determine chemical composition. X-ray diffractometer (Bruker D8 advance) was employed to analyze crystal phase in WBS powder and WBSG-PES-NMP strips. First, the catalyst sample was grinded before testing, Cu Kα served as light source, the scan scope of x-ray diffractometer was between 10°–60° interval, and x-ray wavelength was 0.15406nm. The cross-sectional surface of WBSG-PES-NMP strips was observed by using SEM (HITACHI S-4800). The surface area of strips was characterized by BET analysis (JW-BK200A, JWGB Sci & Tech Corp., China).

About the adsorption test, approximately 5.0 g of strip was added to 500 mL of multi-metal ion solutions (20 mg/L of each Fe²⁺ and Cu²⁺ ions, 40 mg/L of Mn²⁺) at 25 °C. The sample bottles were stirred at the speed of 200 r/min for 2 h-48 h and filtered through the filter paper. The residual concentration of heavy metal ions in solutions was determined using atomic absorption spectroscopy (ContrAA 700, Yena, Germany). The adsorption amount of WBSG-PES-NMP strip with each heavy metal ions was calculated.

3. Results and discussion

3.1. XRD analysis

Figure 3. shows the XRD analytical results of specimens of WBSG and WBS respectively. 2θ ranges between 10° and 60°, which indicates that these materials are in an intermediate state between
amorphous state and semi-crystalline state. Both amorphous and crystalline phases are presented in XRD pattern of WBS powder. A broad peak in the region of 20–30° and 12–20° was found in WBS powder and WBSG respectively. It’s revealed in the figure that Mullite peak is the main peak of WBS geopolymer powders. In addition, the appearance of SiO₂ crystalline peak, thereby improving the compressive strength of geopolymer specimens. Other crystalline peaks are consisted of silimanite and magnetite.

3.2. SEM analysis

SEM micrographs of WBSG-PES-NMP strips revealed the porous structure and the WBSG powder was surrounded by PES as shown in Figure 4 and Figure 5. The outer round of WBS geopolymer strip appeared the little finger-like structure of pores (Figure 4) and the core of WBS geopolymer strip showed the sponge structure of pore (Figure 4). In addition, quantity of geopolymeric gel directly affects the binder’s adsorption of heavy metal ions. The geopolymeric gel in the WBSG-PES-NMP has a higher surface area and a bigger pore volume.

These results prove that the resultant of geopolymeric reaction, and amorphous geopolymer gels are the main products of the mixture of WBS. These observations also agree well with XRD results. In addition, after heavy metal adsorbing, quantity of pores appeared reducing, and some fine particles block up the pores of WBSG. These results prove that the resultant of higher surface area and a bigger pore volume, and amorphous geopolymer gels are the main reasons to capture heavy metal ions in water.
3.3. BET analysis
The BET analysis results of WBS and WBSG are listed in Table 2, which show the geopolymeric gel based WBSG has large surface area and pore volume, small pore diameter. These superiorities all contribute to absorbent reaction.

Table 2. BET results of WBS and WBSG.

| No. | Surface area/m²·g⁻¹ | Pore volume/cm³·g⁻¹ | Pore diameter/nm |
|-----|---------------------|---------------------|------------------|
| WBS | 1.547               | 0.006               | 14.843           |
| WBSG| 52.983              | 0.104               | 7.840            |

3.4. Heavy metal absorbing analysis
For determining the performance of WBSG-PES-NMP strip, adsorption capacities of each heavy metal were measured as a function of adsorption time. When the WBSG-PES-NMP strip was added into the multi heavy metal solution, the adsorption time was settled as 0 h; the results are shown in Table 3 and Figure 6.

The amount of adsorbed heavy metal ions increased with the increment of contact time and reached adsorption equilibrium after 24 hr. The geopolymer adsorbed heavy metal cations in order of Mn²⁺ > Cu²⁺ > Fe²⁺. Moreover, from the adsorbing process photos, we can simply find the adsorption capacity of WBSG-PES-NMP strip against the adsorption time. Therefore, the results suggested that it is suitable to describe the adsorption of heavy metal ions on WBSG-PES-NMP strip. It can be concluded that WBSG-PES-NMP strip adsorbed heavy metal ions by the chemisorption mechanisms, electrostatic attractions and Var der Waals adsorption which control the monolayer and multilayer adsorptions.

Table 3. Adsorption capacity of WBSG-PES-NMP strip toward Fe²⁺, Cu²⁺, Mn²⁺ with adsorption time, %.

| Number | 0 h | 2 h | 5 h | 8 h | 12 h | 24 h | 48 h |
|--------|-----|-----|-----|-----|------|------|------|
| Fe²⁺   | 0   | 26.1| 35.3| 45.2| 50.8 | 53.9 | 56.8 |
| Cu²⁺   | 0   | 32.5| 43.2| 50.3| 58.5 | 60.9 | 63.2 |
| Mn²⁺   | 0   | 60.2| 67.8| 75.3| 78.0 | 85.6 | 88.4 |

4. Conclusion
WBSG-PES-NMP strip were successfully prepared through phase transition method in the laboratory. In the polymer matrix, geopolymer particles were embedded with porous structures. The strips were easier to treat and handle for heavy metal adsorption application compares to PES-NMP strips. In addition, WBSG-PES-NMP strip exhibited the high removal efficiency for Fe²⁺, Cu²⁺, Mn²⁺.
WBSG-PES-NMP strip may be used as an heavy metal adsorbent for suitable waste water and heavy metal ions adsorption application.

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