Experimental Study on the Use of Highway Tunnel Spoil as Artificial Wetland Fill

Yufeng ZHUa,b, Bochang DONGa,b,1, Jun YUa,b and Dongrui LIa,b

a RIOH High Science and Technology Group Co., Ltd, Beijing 100088, China
b Research Institute of Highway Ministry of Transport, Beijing 100088, China

Abstract. In view of the large amount of tunnel slag in mountainous areas and the difficulty of selecting sites for slag sites, an experimental study on the use of tunnel slag as substrate filler for artificial wetlands was conducted on the section of G8513 Pingliang-Mianyang National Highway from Wudu to Jiuzhaigou (Gan-Chuan border). Based on the support effect of tunnel slag on artificial wetland plants and the provision of surface for microorganisms to grow, the tunnel slag was modified to further reduce the concentration of total phosphorus and ammonia nitrogen in water bodies through adsorption. This study makes full use of the value of slag as a resource, eliminates the negative environmental impact of traditional slag treatment, and also alleviates the eutrophication problem caused by excessive nitrogen and phosphorus in the water body at the same time.

Keywords. Highway, tunnel spoil, artificial wetland, experimental study

1. Introduction

With the increasing number of mountain roads in China, the amount of road tunnel slag disposal is gradually increasing. The traditional tunnel slag disposal method is mainly to build a slag site, fill and roll the tunnel slag, and finally carry out surface restoration, without resourceization of the slag, but simply pile up the landfill, resulting in a large amount of waste of resources. At the same time, the high tunnel than the highway project is located in the high mountain valley section, the terrain is steep, the site of the dump site is very difficult, may also have a negative impact on the local natural ecosystem. In addition, the individual slag dump exists in place of grinding, loose structure and other circumstances, in the rainstorm effect is very easy to destabilize, and even induce landslides, mudslides and other disasters. Especially when the slag dump is located in the upstream of residential sites, important structures, etc., it poses a major threat to people’s lives and property safety. Therefore, the disposal of a large number of abandoned slags is no longer simply an engineering problem, but also involves environmental protection, soil and water conservation, the safety of the masses’ property, highway operation safety and other issues.

Artificial wetlands purify wastewater through synergistic physical, chemical and biological processes [1]. The matrix filler of artificial wetlands is the basic unit for its rooting plants, fixing functional microorganisms, and adsorbing nitrogen and phosphorus pollutants. Artificial wetland matrix filler should be reasonably selected according to the

1 Corresponding Author, Bochang DONG, RIOH High Science and Technology Group Co., Ltd, Beijing 100088, China; Email: 448946437@qq.com.
different water quality requirements of different regions, the difficulty of obtaining materials and other conditions, and consider a reasonable ratio of matrix filler. Most of the artificial wetland matrix filler options are based on natural minerals or their modified materials, focusing on strengthening their adsorption capacity, making the filler as an artificial wetland matrix, with better adsorption capacity, more suitable as an immobilization carrier for microorganisms.

2. Mineral Composition and Structural Analysis of Tunnel Rejects

2.1 Experimental Method

(1) Sample pre-treatment
After the initial crushing of the large tunnel rejects from G8513 Pingliang-Mianyang National Highway from Wudu to Jiuzhaigou (Gan-Chuan border), they were placed into the crusher for 30 seconds to obtain the slag powder. The characterization sample was obtained by passing through 200 mesh sieves.

(2) Characterization analysis
We take 2g of the sample pressed and processed, and the sample components were characterized using X-ray fluorescence spectrometry (Zetium, PANalytical, Netherlands) to obtain the mass percentages of each element. Another 2 g of sample was pressed and processed, and the structure of the sample was characterized by powder X-ray diffractometer (X-Pert3 Powder, PANalytical, Netherlands) with a test angle range of 5-90° and a test time of 20 min. The raw data were processed by MDI Jade 6 software and the peaks with FOM value less than 10 were identified to identify the crystal structure in the sample.

2.2. Mineral Composition of Tunnel Rejects

The results of X-ray fluorescence spectroscopy showed that Si elements, except O elements, accounted for the highest percentage of tunnel rejects, which could reach more than 30%, followed by Al and Fe elements, which were in the range of 5%-10%. Elements with a content of 1%-5% include K, Ca and Mg. The other elements are below 1%. It can be seen that the main component of the tunnel rejects is silica or metal aluminosilicate.

2.3. Mineral Structure of Tunnel Rejects

The characterization results of X-ray fluorescence spectrometer and X-ray diffractometer showed that the tunnel rejects consisted mainly of a large amount of quartz and some chlorite and muscovite. According to literature research, these three main components have no significant adsorption effect on ammonia nitrogen and total phosphorus in the aqueous environment, and they have small specific surface area and no special pore structure, which makes them unsuitable for direct use as adsorbent materials [2, 3]. Therefore, a reasonable modification of this tunnel reject is needed to enhance its adsorption and removal capacity for pollutants.
3. Modification and Adsorption Effect of Tunnel Rejects

In this study, both acid and alkali etching were used to enrich the surface of the slag. According to literature findings, Fe-based materials have a good adsorption capacity for total phosphorus [4]. In this study, the modification of tunnel slag was attempted using Fe oxides and Fe-based Layered Double Hydroxide (LBDH). As for ammonia nitrogen adsorption, it is more difficult to adsorb on the material surface due to the characteristics of ammonium ions, and the current ammonia nitrogen adsorption materials reported in international journals are bentonite, montmorillonite and zeolite, so bentonite was used in this study as the material for ammonia nitrogen adsorption modification.

3.1. Experimental Method

(1) Surface activation

The tunnel rejects were crushed to 3-5 mm, washed and dried with ultrapure water. The 3-5 mm tunnel slag was soaked in 1.0 mol/L HCl solution for 24 h (solid-liquid ratio 1:5), then rinsed repeatedly with distilled water to neutral and dried in an oven at 90°C to obtain acid-treated tunnel slag (ACTS). Another part of the washed and dried 3-5 mm tunnel slag was soaked in 1.0 mol/L NaOH solution for 24 h (solid-liquid ratio 1:5), then it was rinsed repeatedly with distilled water and dried in an oven at 90°C to obtain alkali-treated tunnel slag (ALTS).

(2) Surface modification

ACTS and ALTS were placed in 0.1 mol/L FeCl₃ solution (solid-liquid ratio 1:5), immersed for 8 h, calcined in a muffle furnace at 200°C for 2 h, then washed with deionized water, immersed in 50 mg/L bentonite solution for 2 min, removed and drained, dried in an electric thermostatic drying oven at 90°C, immersed in 50 mg/L bentonite solution for 2 min, The modified tunnel slag FeACTS1 and FeALTS1 were obtained respectively by taking out and draining the water, and then put into an electric thermostatic drying oven at 90°C again.

ACTS and ALTS were placed in 0.1 mol/L FeCl₃ solution (solid-liquid ratio 1:5), adjusted the pH to 10 with 1.0 mol/L NaOH solution, stirred strongly for 30 min, soaked for 8 h, calcined in a muffle furnace at 200°C for 2 h, then washed with deionized water, dried in an electric thermostatic drying oven at 90°C, immersed in 50 mg/L bentonite solution for 2 min, removed and drained, and then put into an electric thermostatic oven for drying at 90°C again to obtain modified tunnel slag FeACTS2 and FeALTS2, respectively.

ACTS and ALTS were placed in 0.1 mol/L FeCl₃ solution (solid-liquid ratio 1:5), soaked for 8 h, taken out and washed with deionized water 5-6 times to remove the solid surface ions, put into an electric thermostatic drying oven at 105°C to dry, soaked in 50 mg/L bentonite solution for 2 min, taken out and drained, then put into an electric thermostatic oven for drying again at 90°C to dry, respectively Modified tunnel slag FeACTS3 and FeALTS3 were obtained.

A mixed solution containing 0.05 mol/L FeCl₃ and 0.1 mol/L MgCl₂ (solid-liquid ratio 1:5) was configured, and ACTS and ALTS in the solution were placed for 10 min and soaked for 30 min, then the pH to 11 was adjusted with 1.0 mol/L NaOH solution, with strongly stirring for 30 min and soaking for 8 h. Then the slag was removed and discarded. The modified tunnel rejects FeACTS4 and FeALTS4 were obtained by draining and drying in an electric thermostatic oven at 90°C, soaking in 50 mg/L
bentonite solution for 2 min, removing and draining, and drying in an electric thermostatic oven at 90°C again.

3) Measurement of adsorption kinetic curves
A 20 mg/L solution of PO₄³⁻-P was prepared using sodium hydrogen phosphate, and 50 g of modified tunnel rejects were added to 50 mL of 20 mg/L PO₄³⁻-P solution, placed in a constant temperature shaking chamber at 30°C, and 0.5 mL of the solution was taken at 10 min, 20 min, 40 min, 60 min, 80 min, 100 min, 120 min, 140 min, 160 min, and 180 min to determine the PO₄³⁻-P concentration. The PO₄³⁻-P concentration was determined by ammonium molybdate spectrophotometry (GB 11893-89), and the kinetic curves of the adsorption of PO₄³⁻-P by the modified tunnel rejects were plotted.

A 20 mg/L solution of NH₄⁺-N was prepared using ammonium chloride, and 50 g of the modified tunnel rejects were added to 50 mL of 20 mg/L NH₄⁺-N solution, placed in a constant temperature oscillator at 30°C and shaken, and 0.5 mL of the solution was taken at 10 min, 20 min, 40 min, 60 min, 80 min, 100 min, 120 min, 140 min, 160 min and 180 min to determine the NH₄⁺-N concentration, NH₄⁺-N concentration was determined by the spectrophotometric method of nano reagent (GB7479-87), and the kinetic curves of NH₄⁺-N adsorption by modified tunnel rejects were plotted.

4) Measurement of adsorption thermodynamic curve
A 20 mg/L solution of PO₄³⁻-P was prepared using sodium hydrogen phosphate at 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L, 100 mg/L. 50 g of modified tunnel rejects were added to 50 mL of PO₄³⁻-P solution, placed in a constant temperature oscillator at 30°C and shaken, and the PO₄³⁻-P concentration was determined by taking 0.5 mL of the solution at 6 h. The thermodynamic curves of the adsorption of modified tunnel rejects on PO₄³⁻-P were plotted.

The NH₄⁺-N solutions of 10 mg/L, 20 mg/L, 40 mg/L, 60 mg/L, 80 mg/L and 100 mg/L were prepared using ammonium chloride, and 50 g of modified tunnel rejects were added to 50 mL of NH₄⁺-N solution and placed in a constant temperature shaking chamber at 30°C. The NH₄⁺-N concentration was determined by taking 0.5 mL of the solution at 6 h. The thermodynamic curves of NH₄⁺-N adsorption by modified tunnel rejects were plotted.

3.2. Adsorption Effect and Kinetic Process of Modified Tunnel Rejects

The results of the adsorption kinetic experiments showed that the original rejects had no significant adsorption of PO₄³⁻-P and NH₄⁺-N. Among a total of eight modification schemes tried in this study, FeACTS4, the modified slag obtained from the acid-etched slag Fe/Mg layered bimetallic hydroxide composite bentonite modification scheme, had the best PO₄³⁻-P and NH₄⁺-N adsorption effects [5]. Therefore, it was used as the final tunnel slag modification scheme in this study.

3.3. Thermodynamic Processes for the Adsorption of PO₄³⁻-P and NH₄⁺-N by Modified Tunnel Rejects

To further clarify the adsorption processes of FeACTS4 on PO₄³⁻-P and NH₄⁺-N, the adsorption thermodynamic curves of FeACTS4 on PO₄³⁻-P and NH₄⁺-N were plotted in this study, and the Langmuir and Freundlich adsorption thermodynamic equations were fitted.

The fitting results show that the Langmuir adsorption isotherm is more suitable to describe the adsorption process of PO₄³⁻-P and NH₄⁺-N on FeACTS4 than the Freundlich
equation [6, 7]. From this, it is known that the adsorption of PO$_4^{3-}$-P and NH$_4^+$-N on FeACTS4 occurs as a single molecular layer, and the maximum adsorption of FeACTS4 on PO$_4^{3-}$-P and NH$_4^+$-N can be calculated as 25.4 mg/kg and 11.8 mg/kg, respectively.

4. Characterization of Modified Tunnel Rejects

4.1. Experimental Method

(1) Sample pre-treatment
The lumped FeACTS4 was placed into the pulverizer for 30 seconds to obtain the discarded powder. The characterization sample was obtained by passing through 500 mesh sieves.

(2) Characterization analysis
We take 2g sample into a centrifuge tube, dried and stored, on an X-ray photoelectron spectrometer (AXIS Supra, Kratos Analytical Ltd., British) to obtain the binding energy spectra of each element. The energy spectra were analyzed using CasaXPS software, and the C-element peaks were calibrated to 484.8 eV. All the elemental peaks were split and the individual peaks were compared in the NIST database to obtain the elemental morphology data. After that, the peak area of each peak was calculated and the ratio of each element was calculated by sensitivity factor.

The samples were taken and mixed with spectrally pure KBr and ground for compression, and characterized on a Fourier transform infrared spectrometer (nicolet is 50, ThermoFisher, America) to test the absorption peaks in the mid-infrared (150-900 cm$^{-1}$) range to obtain infrared spectral images.

The sample structure was characterized by powder X-ray diffractometer (X-Pert3 Powder, PANalytical, Netherlands) in the range of 5-90° with a testing time of 20 min. The raw data were processed and the peaks were identified by MDI Jade 6 software, and the peaks with FOM value were less than the raw data processed by MDI Jade 6 software and the peaks with FOM value less than 10 were identified to identify the crystal structure in the sample.

4.2 Composition characteristics of FeACTS4

The Fourier transform infrared spectra of the original rejects as well as FeACTS4 are shown in Figure 1. Mg and Na increased while Al decreased. The increase in Fe content is attributed to the formation of Fe/Mg layered bimetallic hydroxide, while the increase in Na content is due to the addition of bentonite and the increase in Mg benefits from both. the decrease in Al relative content is attributed to the dissolution of aluminosilicate due to acid etching.

4.3. Structural Characteristics of FeACTS4

The results of the characterization of FeACTS4 by X-ray diffractometer are shown in Figure 2. This result proves that the structures of chlorite and hydrated calcium magnesium oxide were removed during the acid etching process, while the structures of quartz and muscovite were not completely removed because of their strong acid
resistance, resulting in the main mineral structures of FeACTS4 being quartz and muscovite.

![Figure 1. Fourier transform infrared spectra of the original rejects and FeACTS4.](image1)

![Figure 2. X-ray diffraction pattern of tunneling reject sample of FeACTS4.](image2)

5. Conclusion

In this study, the components and structures of tunnel rejects from G8513 Pingliang-Mianyang National Highway from Wudu to Jiuzhaigou (Gan-Chuan border) were characterized by X-ray fluorescence spectrometry and X-ray diffractometry [8], and it was clear that elemental silicon was the main element in the rejects, containing some silica-aluminates, and the main components of tunnel rejects were quartz, chlorite, hydrated calcium magnesium oxide, and white mica. According to the components and structural characteristics of the tunnel slag, two schemes of acid and alkali etching were used to activate the surface of the slag, and four different schemes were used to synthesize iron-based adsorbents on the surface of the slag. The adsorption kinetics of $\text{PO}_4^{3-}$-$\text{P}$ and $\text{NH}_4^+$-$\text{N}$ were investigated by adsorption kinetics experiments with a total of eight different modification schemes. The chemisorption process mainly occurred on FeACTS4. The adsorption thermodynamics experiments showed that the adsorption processes of $\text{PO}_4^{3-}$-$\text{P}$ and $\text{NH}_4^+$-$\text{N}$ on FeACTS4 were in accordance with the Langmuir adsorption isotherm model, and the adsorption processes on the surface of FeACTS4 were monolayer adsorption processes with the maximum adsorption amounts of 25.4
mg/kg and 11.8 mg/kg, respectively. Characterisation by X-ray diffraction showed that the chlorite and hydrated calcium magnesium oxide structures were removed by acid etching during the modification process, while Fe/Mg layered bimetallic hydroxide and bentonite structures were present in FeACTS4.

In this study, the modified tunnel slag was successfully modified, so that the modified slag has strong PO$_4^{3-}$-P and NH$_4^+$-N adsorption capacity, which is suitable for resource recycling as artificial wetland substrate, solving the problem of difficult resource utilization of tunnel slag.

References