Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(4):754-761

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Adsorption of phenol on acid-treated slag wastes in waste water

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ABSTRACT

This study investigates the liquid-phase adsorption behavior of phenol form waste water by using slag, which is one of the solid wastes from steel refining process. This adsorption technique is one green process based on using the slag waste as adsorber for removing organic contaminants from waste water. First, the raw slag was chemically treated by different concentrations of sulfuric acid, and then the removal efficiencies of phenol by treated slag were examined at various pH values. The adsorption isotherms and adsorption kinetics show the adsorption performance of phenol on the treated slag adsorbers. Experimental results deliver the best removal efficiency of phenol on the slag can achieve at pH = 6−8. Two famous adsorption models, Freundlich and Langmuir equations, were adopted to analyze the liquid-phase adsorption behavior, showing good correlations to the experimental data. The merit of the present work is to shed some lights on (i) the treated slag displays a promising candidate as high-performance adsorber for organic removal, and (ii) the exhausted slag could be recycled and served as controlled low-strength material (CLSM). The LCSM not only removes organic compounds but also uses as fillers for construction, which opens novel application in environmental protection field.

Keywords: Slag, Phenol, Adsorption, Controlled Low-Strength Material (CLSM)

INTRODUCTION

Phenolic compound and its derivatives are often seen in waste water, and thus adsorption capacity of the phenolic compounds is one of the crucial factors in evaluating carbon adsorbents [1]. In fact, the phenolic compounds are known to be toxic organics, and they frequently exist in industrial waste water, e.g., oil-refining, petrochemistry, coke making, and bakelite [2]. So far, waste-water treatments such as biological, physical adsorption, and chemical oxidation treatments, are generally recognized to remove the organics and heavy metals from waste water [3-5]. Due to its large consumption of chemical agents, the chemical-based treatment possesses some disadvantages such as expensive cost and second pollution. Accordingly, the liquid-phase adsorption technique has been widely used in waste-water treatments, confirmed by pioneering studies [6-10]. It is known that slag is one of the solid wastes after steel refining process, and the raw slag can be used as construction materials including architecture aggregate for roadway and cement/concrete, controlled low-strength material (CLSM), and so on [11]. Because of its honeycomb porosity and high surface area, the raw slag offers somewhat adsorption capability, showing the replacement for activated carbon, silica gel, and alumina adsorbents. Previous studies have reports its removal ability for various organic compounds and heavy metal ions from waste water [12,13]. Using the slag as adsorbents for removing organics from waste water is an eco-environmentally green technique due to cost-saving and total solution for environmental protection and waste reuse. Additionally, the adsorption behavior on fly ash and slag strongly relates to their surface area and surface compositions such as Al, Mg, Fe, and Zn [14-17]. However, the adsorption of organics onto the slag still requires a better understanding, and there are few reports concerning this research field, to the best of our knowledge.

This study intends to figure out the adsorption kinetics of phenol (C_6H_5OH, molecular weight: 94) onto the slag solids. The equilibrium adsorption isotherms were well characterized by using Freundlich and Langmuir models, and their correlations with experimental data and prediction curves were discussed. The adsorption capacity for phenol can serve as an important indicator for the adsorption of polar aromatic compounds of small sizes. Accordingly, the merit of the present work is to shed some lights on (i) the treated slag displays a promising candidate as high-performance adsorber for organic removal, and (ii) the exhausted slag could be recycled and served as controlled low-strength material (CLSM), showing novel application in environmental protection field.

EXPERIMENTAL SECTION

Acid treatment on slag solids and their characterization

The slag solids used herein were obtained from Dragon Steel Co. (Taichung, Taiwan). The acid-treated process of raw slag could be described as follows. First, the raw slag was dried to remove moisture at 105°C, and then the dried slag was grounded and sieved, ensuring uniform particle size of 120 μm. After that, 5 g slag powder was slowly poured in 0.2 M sulfuric acid and then stirred for 0.5 hr. This acid-treated process enabled the creation of more surface area for liquid-phase adsorption. The slag sediment was then washed by using distilled water twice and dried at 105°C overnight. The morphological observation of acid-treated slag powders was characterized by field-emission scanning electron spectroscopy (FE-SEM, JEOL JSM-5600) and transmission electron microscopy (TEM, JEOL JEM-6500F). The crystalline structure of the slag powders was investigated by using X-ray diffraction (Shimadzu Labx XRD-6000) with Cu−Kα source.

Static liquid-phase adsorption

The phenol solution (1000 mg L^{-1}) was prepared by diluting the adsorbates in distilled water. Adsorption experiments were performed by placing a certain amount of slag adsorbents and 100 cm^3 of the prepared aqueous solution into a 250 cm^3 glass-stoppered flask. The isothermal adsorption experiments using dried slag powders as adsorbent were carried out at 30°C in a shaking water bath with rotation speed of 200 rpm. The pH values of slag slurries were then adjusted to 5, 6, 7, 8, 9, and 10 by using 0.5 M HCl and 0.5 M NaOH. After reaching adsorption equilibrium (i.e., 12 hr), all samples were passed through nylon filters prior to analysis in order to minimize the interference of slag fines with the analysis. The phenol concentrations were analyzed by ultraviolet/visible spectroscopy (Shimadzu, Model UV-2550) at a fixed wavelength of 268 nm. The amount of adsorbate captured by the slag adsorbents was determined as follows:

$$Q_\mathrm{e} = \frac{(C_\mathrm{i} - C_\mathrm{e})V}{M} \tag{1}$$

where Q_e is the amount of adsorbate on the slag at equilibrium, C_i is the initial concentration of phenol in the aqueous solution, C_e is the residual concentration, V is the volume of the aqueous solution, and M is the amount of acid-treated slag used in the adsorption.

RESULTS AND DISCUSSION

Morphology and chemical composition of slag adsorbents

Figures 1 and 2 show FE-SEM micrograph of the treated slag powders, respectively. The micrograph clearly reflects that the slag displays a rough surface, which is constructed by tiny particles and cavities. The rough surface is capable of creating a large number of surface areas, possibly benefiting for adsorption capacity of phenolic compounds. As observed from the FE-SEM image, the slag powders are mainly porous, and its porosity can achieve as high as 50–60%. The vast porosity is, thus, believed to show an enhanced adsorption performance. Since it contains 10–30 wt% carbon content, the slag retains the properties of activated carbon, offering a strong affinity to adsorb organic contaminants, heavy metals, and suspended colloids in waste water. It is well known that the favorable adsorption would take place when the pore size of adsorbers is 2–3 times larger than the molecular size of adsorbate [18]. Since organic molecular diameters are estimated to be 0.16–0.8 nm, the porous slag powders are better potential candidates for removing the phenolic compounds from waste water. This is because the slag powders provide a well-developed pore size distribution, consisted of micro-, meso-, and macropores.

The energy-dispersive x-ray spectroscopy (EDS) pattern of the slag is illustrated in Figure 2, confirming the presence of C, O, Si, A1, Mn, Ca, Fe, and Zn elements. The chemical composition of the slag is listed in Table 1. It can be seen that there almost no negative ions, and oxygen content plays the highest portion among these elements. This can be attributed to the existence of metal oxide and silica in the treated slag powders.

The typical XRD pattern of the treated slag is depicted in Figure 3, which has been carefully compared to standard JCPDS pattern. This pattern explicitly reveals the presence of C and FeO. Three main peaks of FeO appear at 41.725°, 35.927°, and 60.482°, assigned to (200), (111), and (220) reflections of dace-centered cubic. This result proves that the slag powder is mainly composed of crystalline carbon and FeO.

Effect of pH value on adsorption performance

According to the previous EDS analysis, several types of metal oxides including $A1_2O_3$, MnO, CaO, Fe_2O_3, and ZnO coexist in the slag powders. The presence of metal oxides enables an increase in the pH of waste water, thus affecting the ionization of phenol solution. Therefore, it is necessary to figure out the influence of pH value on the removal efficiency of phenol from waste water. As shown in Figure 4, the removal efficiency is a decreasing function of pH value. This result implies that the adsorption operation of slag at lower pH value exhibits better removal efficiency of phenol in liquid phase, i.e., the adsorption becomes more favorable in acidic solution. This enhanced removal efficiency can be ascribed to the fact that these metal oxides (e.g., CaO, MgO, Fe_2O_3, and $A1_2O_3$) can be leached from the slag and then neutralize with acidic matters, raising the alkalinity of waste water. Herein the phenol adsorbates possess hydrophilic and hydrophobic groups, having strong adsorptive affinity to non-polar and polar adsorbents. The adsorption affinity becomes more evident in acidic solution. Accordingly, the adsorption experiments of phenol onto the slag adsorbents were operated within the pH value of 6–8.

Additionally, two main components, SiO_2 and $A1_2O_3$, are one of the aluminosilicates that offers adsorptive activity to organic compounds. Generally, the aluminosilicates are inactive after a slowly cooling process from high temperatures. Thus, the opened cavities of slag are easily hindered and filled with these oxides, forming a number of closed voids. However, these oxides can be dissolved from the slag solids in acidic solutions. Meanwhile, the closed voids are open, and the opened voids would provide a large amount of active sites for adsorption of phenol in acidic waste water, as demonstrated by Figure 4.

Adsorption isotherm and model prediction

The adsorption kinetic curve for the phenol adsorbed by the slag powders at 30°C is depicted in Figure 5. The adsorption experiment was performed using 1000 mg L^{-1} at pH = 6–8. The kinetic curve shows a rapid uptake at initial stage, followed by gradual adsorption equilibrium after 2 hr. At initial stage, the phenol uptake occurs on the surface and macropore of slag powders due to small diffusion resistance, leading to fast kinetics. With increasing the adsorption period, the phenol adsorbates tend to diffuse through from the macropores and mesopores to interior micropores via concentration gradient. Meanwhile, the mass transfer rate becomes slow because the pore diffusion is the rate-determining step during the whole adsorption process. The equilibrium adsorption of phenol onto the slag at least takes approximately 3 hr, as observed from Figure 5. In this case, the adsorption equilibrium data was collected after the adsorption period of 6 hr to ensure completely adsorption equilibrium. After adsorption equilibrium, it is of interest that the exhausted slag can also be considered as construction material such as CLSM for practical applications, showing a great potential for recycling and environmental friendly.

Two two-parameter isotherm equations, Freundlich and Langmuir, are adopted to describe the adsorption behavior of phenol onto the treated slag powders in the preceding section. The empirical model, Freundlich equation, can be formulated by [19]

$$Q_{\mathrm{e}} = K_{\mathrm{F}}(C_{\mathrm{e}})^{1/n} \tag{2}$$

where K_F and n are empirical constants that determine the curvature and steepness of the isotherm. The above formula can be rewritten to [20-22]:

$$\ln Q_{\mathrm{e}} = \ln K_{\mathrm{F}} + \frac{1}{n}\ln(C_{\mathrm{e}}) \tag{3}$$

Herein the linearity plot of ln Q_e versus ln C_e would give the value of n and K_F from the slope and the intercept, respectively. The linear plot is illustrated as Figure 6, and these Freundlich parameters are collected and listed in Table 2. The linear correlation factor (r^2) can reach as high as 0.9818, implying good fitting to the experimental data. The prediction curve, based on the Freundlich model, is present to well describe the adsorption behavior, as shown in Figure 7.

The other famous two-parameter equation is the Langmuir equation, which is expressed as [20-22]

$$Q_{\mathrm{e}} = \frac{Q_{\mathrm{L}} K_{\mathrm{L}} C_{\mathrm{e}}}{1 + K_{\mathrm{L}} C_{\mathrm{e}}} \tag{5}$$

where Q_L is the amount of adsorbate adsorbed per unit mass of slag corresponding to complete monolayer coverage, and K_L is the Langmuir constant, which can be considered as a measure of adsorption energy [23]. Again, a linear plot of (C_e/Q_e) against C_e was used to give the values of Q_L and K_L from the slope and intercept of the plot, as shown in Figure 8. The Langmuir parameters are listed in Table 3. The model-fitting results (i.e., r^2: 0.9987) show that the Langmuir model displays a fairly good description of the adsorption behavior, as shown in Figure 7. The maximal monolayer adsorption capacity (Q_L) of phenol onto the slag is achieved as 121.95 mg/g, which is very close to that of commercial activated carbon. Accordingly, the slag is believed to possess a large number of cavities that provide active sites available for the adsorption of phenol adsorbates in liquid phase.

On the basis of the results, both Freundlich and Langmuir isotherms would provide excellent description for the adsorption behavior of phenol onto the slag adsorbents. The smaller $1/n$ value, obtained from the Freundlich equation, the higher adsorption affinity to the phenol adsorbate. Since the $1/n$ value is approximately 0.167 in this case, this means that this is a favorable adsorption within the entire concentration. Such high correlation coefficient (r^2: 0.9987 from Langmuir equation) reflects that the adsorption behavior obeys the basic assumption of monolayer adsorption onto the slag powders, referring to the Langmuir model. This also confirms that the presence of strong affinity between slag surface and phenol adsorbates in liquid phase.

Table 1.Chemical composition of the treated slag by EDS analysis

Element	Weight percentage (%)	Element	Weight percentage (%)
C	25.2	Fe	8.2
O	35.2	Mn	5.2
Ca	8.6	Zn	4.0
Si	8.3	Al	5.0

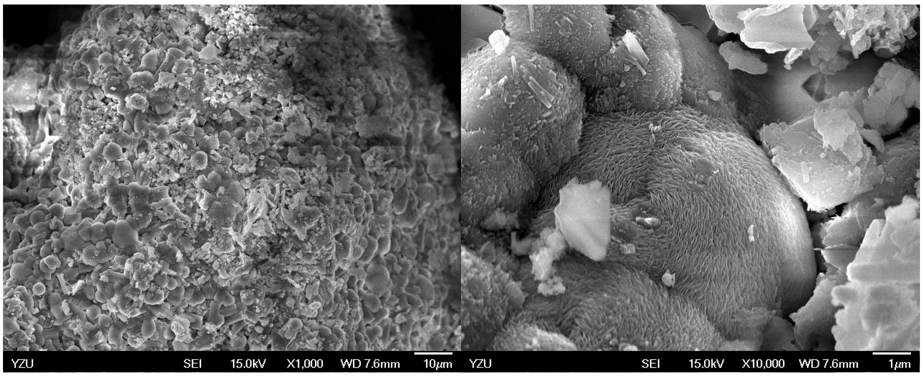

Figure 1.FE-SEM images of the acid-treated slag powders with low (left) and high (right) magnifications
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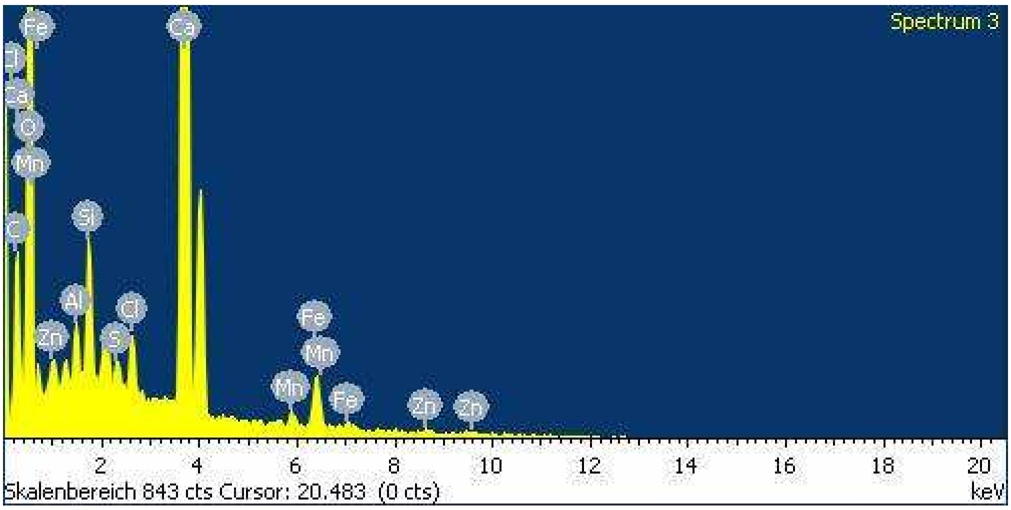

Figure 2.EDS spectrum of the acid-treated slag powders
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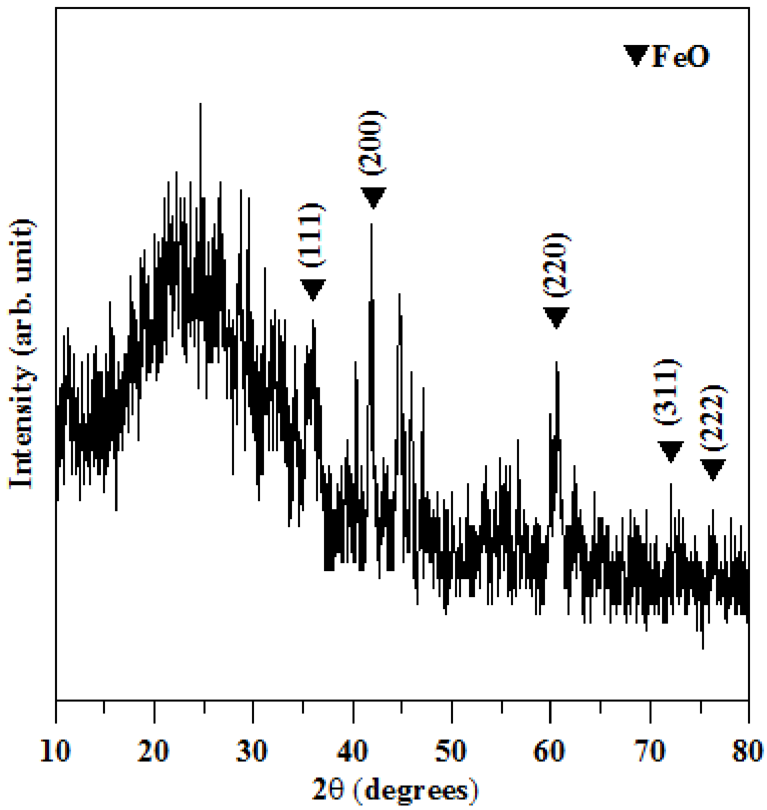

Figure 3.Typical XRD pattern the acid-treated slag powders
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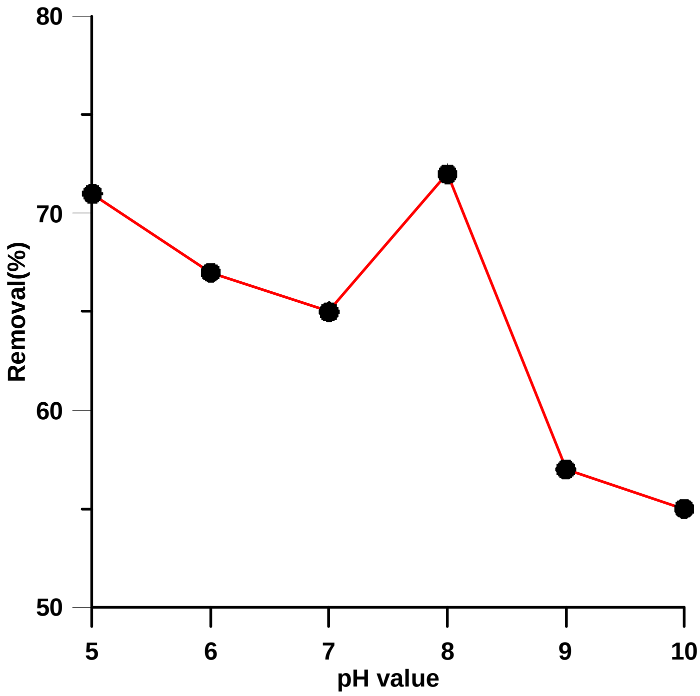

Figure 4.Variation of removal efficiency with pH value for removal of phenol on acid-treated slag powders
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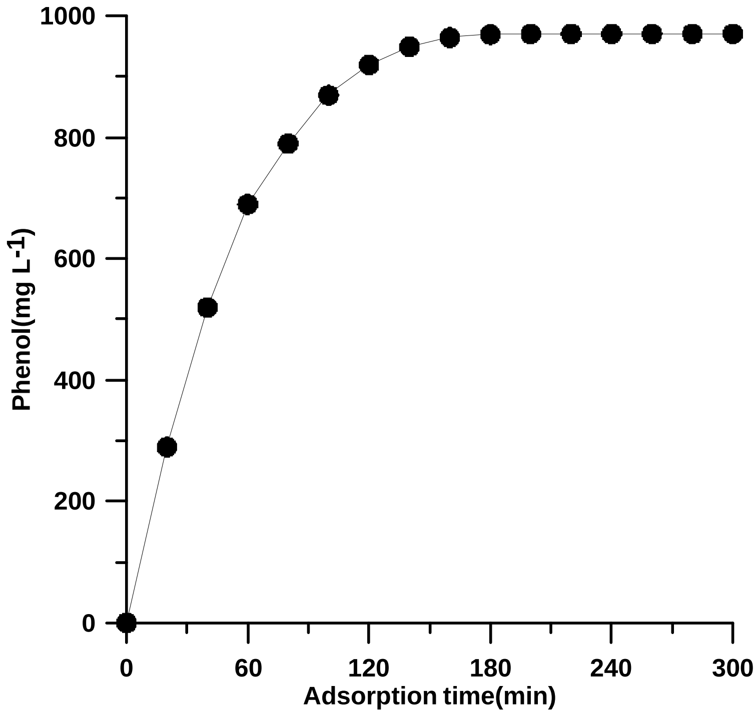

Figure 5.Adsorption kinetics of phenol the acid-treated slag adsorbent at 30°C
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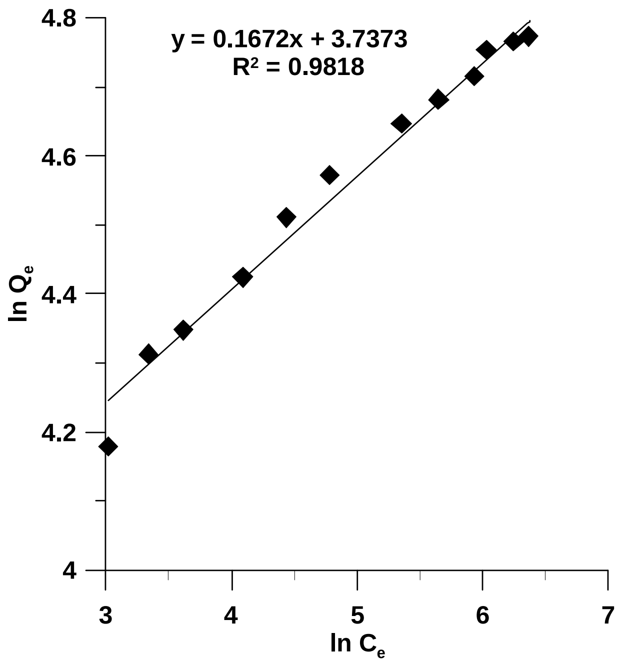

Figure 6.Linear Freundlich plot for adsorption of phenol on the acid-treated slag at 30°C
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Table 2.The parameters of Freundlich isotherm for adsorption of phenol onto the treated slag adsorbents at 30°C

Adsorbent	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	n	r^2
Slag	41.98	5.98	0.9818

Table 3. The parameters of Langmuir isotherm for adsorption of phenol onto the treated slag adsorbents at 30°C

Adsorbent	Q_L (mg g^{-1})	K_L (L mg^{-1})	r^2
Slag	121.95	0.0038	0.9987

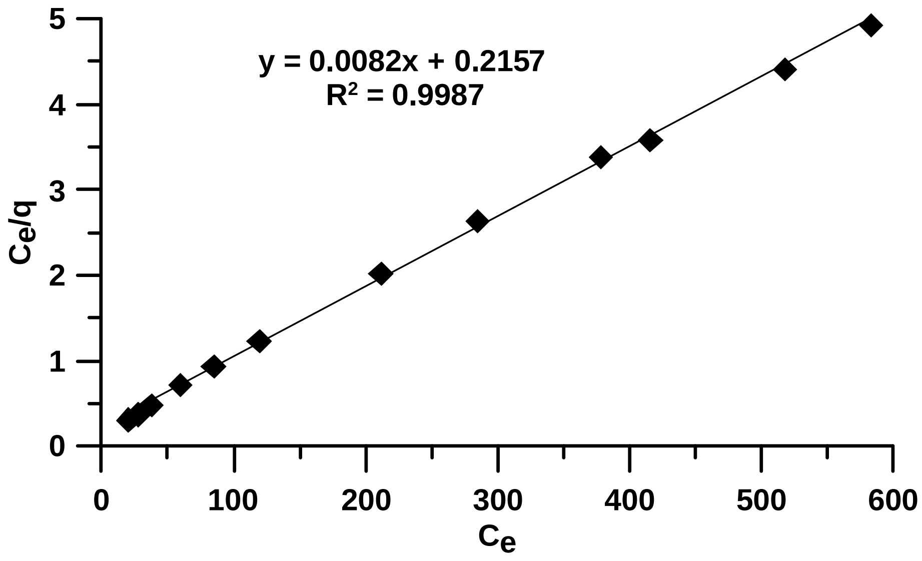

Figure 7.Linear Langmuir plot for adsorption of phenol on the acid-treated slag at 30°C
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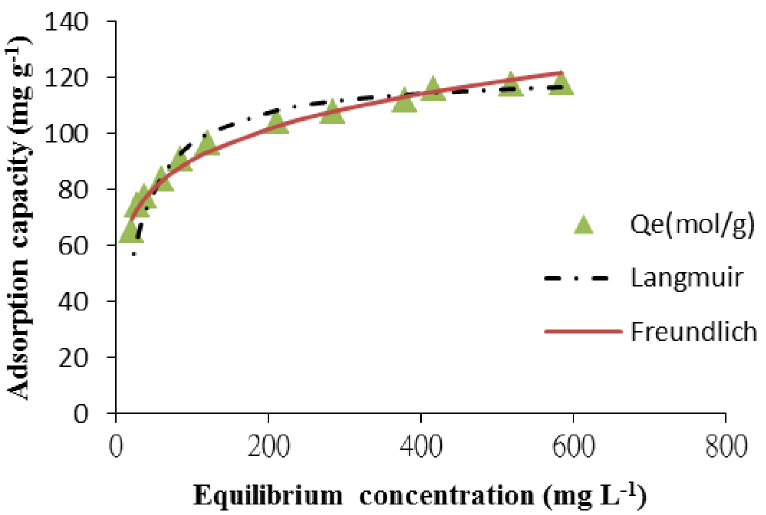

Figure 8.Adsorption isotherm of phenol on the acid-treated slag at 30°C, in which the solid symbols are experimental data and two prediction curves are Langmuir and Freundlich equations
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CONCLUSION

This study investigated that the adsorption of phenol onto the slag powders, prepared from high-temperature and high-pressure sintering process. The slag powders were chemically treated by sulfuric acid, creating rough surface that consisted of tiny pellets and cavities. The rough surface of slag enabled the formation of more active sites for adsorption of phenol in liquid phase. That is, the higher surface area and the smaller particle size of slag, the higher adsorption capacity of phenol could be achieved. The experimental results also confirmed that the optimal pH value is set at 6–8 for higher removal efficiency of phenol from waste water. Both Freundlich and Langmuir models displayed good fitting result to the adsorption behavior, according to excellent correlation coefficient of > 0.98. This result could be attributed to strong interaction between adsorbates and slag surface, inducing high removal efficiency of phenol in liquid phase. Due to its high removal efficiency, the spent slag powders could serve as one kind of the construction materials, e.g., CLSM. This usage of the slag could serve not only for high-performance adsorbents for removing organic compounds but also use for LCSM application, showing a great feasibility for commercialization due to its simplicity, convenience, and recycling use.

Acknowledgments
The authors are grateful for the financial support from the Yu Song Technology Co. under the contract No.

RD1010307.

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