


Article

Phosphate Removal from Secondary Effluents Using Coal Gangue Loaded with Zirconium Oxide

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Abstract: Phosphorus from secondary effluents and coal gangue from coal mining have caused serious environmental problems. The feasibility of phosphate removal from secondary effluents using calcinated coal gangue loaded with zirconium oxide (CCG-Zr) was explored. Major influencing factors like the calcinated temperature, CCG-Zr ratio, adsorbent dose, time and solution pH, etc. were investigated. Newly developed CCG-Zr accomplished a significantly higher phosphate removal for phosphate (93%) compared with CCG (35%) at a calcinated temperature of 600 °C and CCG-Zr mass ratio of 1:1. For CCG-Zr the maximum phosphate removal rate (93%) was noted at an initial phosphate concentration of 2 mg/L within 20 min. The CCG-Zr displayed a higher phosphate removal rate (85–98%) over a wide range of solution pH (2.5–8.5). The adsorption isotherms fitted better to the Freundlich ($R^2 = 0.975$) than the Langmuir model ($R^2 = 0.967$). The maximum phosphate adsorption capacity of the CCG-Zr was 8.55 mg/g. These results suggested that the CCG-Zr could potentially be applied for the phosphate removal from secondary effluents.

Keywords: low concentration phosphate; phosphate adsorption; coal gangue modification; wastes reuse

1. Introduction

Phosphorus is a limiting nutrient for algal growth and its excessive concentration in wastewater discharged into aquatic environments often causes serious eutrophication problems, namely harmful algal blooms, depletion of dissolved oxygen and decline of aquatic life, etc. [1,2]. The secondary effluents from a typical sewage treatment plant may contain 1.0–2.0 mg/L Phosphorus in an anaerobic-anoxic-oxic (A^2/O) process [3], which contributes to eutrophication in the receiving water bodies [4]. Phosphorus in the secondary effluents is mostly present as phosphate. Consequently, phosphate needs to be removed from secondary effluents to control eutrophication of the receiving water bodies. The control of phosphate in secondary effluents has been widely investigated. Great attention has been paid to the utilization of industrial wastes or their modification for phosphate removal. Iron oxide tailings [5], lanthanum-doped mesoporous SiO_2 [6], iron-nanoparticles-loaded *Spondias purpurea* seed waste [7], steel slag coated with sodium hydroxide [8], alum [9] and other waste materials or their modifications have been explored so far. The major advantages of using these wastes or their modifications for wastewater treatment are cost effectiveness and desired reuse.

Coal gangue is one of the major solid wastes produced as a result of coal mining and its washing. Generally, the total discharge capacity of coal gangue can reach up to 10–15% of the total raw coal extraction [10]. In China, approximately 315 million tons of coal gangue is produced on annual basis, with a total piling of about 4.5 billion tons [11]. Disposal of such a huge quantity of solid waste requires a large landfill area which may also cause serious environmental problems [12–14]. Owing to major chemical constituents, coal gangue possesses SiO_2 and Al_2O_3 with traces of surface Fe and other metals, and thus it may be a potential adsorbent for phosphate. Usually, coal gangue is calcinated for the activation of Al_2O_3 or traces of Fe, etc. metals to enhance phosphate removal efficiencies [15,16]. However, calcinated coal gangue is still uninvestigated as a phosphate adsorbent for its lower phosphate removal efficiencies under calcination. On the other hand, zirconium oxide has been given more consideration for its high sorption selectivity for phosphate and higher resistance against action of acids, alkalis, oxidizing and reducing agents [2,17–23]. Calcinated coal gangue (CCG) modified by zirconium oxide may have better phosphate removal efficiency compared with calcinated coal gangue. However, very limited information is available so far on the phosphate adsorption on calcinated coal gangue modified by zirconium oxide (CCG-Zr). The objective of the present study was the preparation of CCG-Zr by $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratio of 1:1 under different calcinated temperatures (300–800 °C) and various $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratios and testing the prepared material for phosphate adsorption. The effects of various influencing parameters on the phosphate adsorption were also investigated in batch experiments.

2. Materials and Methods

2.1. Materials and Chemicals

Coal gangue samples were obtained from a local coal mining area in China. Zirconium oxychloride ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) with the purity >99.33% was purchased from Zibo Xinlv Yuan Biochemical Co. (Zibo, China). Analytical grade KH_2PO_4 and KCl were used in the experiment.

2.2. Preparation of CCG-Zr

Coal gangue was calcinated at 750 °C in an oven under anoxic conditions for 2 h and passed through a 100-mesh sieve for use [24]. Calcinated coal gangue (100 g) was added to solutions containing different amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ so that different $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratios (0%, 12.5%, 25.0%, 50%, 100%) could be prepared. After 40 h, the calcinated coal gangue was taken out and dried at 90 °C for 2h. The $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratio (50%) was calcinated at different calcinated temperatures (300, 400, 500, 600, 700, 800 °C) for 6 h.

The effect of various calcinated temperatures (300, 400, 500, 600, 700, 800 °C) and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratios (0%, 12.5%, 25.0%, 50%, 100%) on phosphate removal were examined for suitable calcinated temperatures and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ /CCG mass ratios (phosphate adsorptive conditions: 1 g CCG-Zr/50 mL containing 2 mg P/L solution, initial pH 2.5, time: 2 h under 15 °C and 180 rpm).

2.3. Characterization of CCG-Zr and Analysis Methods

The components in calcinated coal gangue (CCG) loaded with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ at different calcinated temperatures were determined by S8 Tiger X-ray fluorescence spectrometers (Germany, Bruker) (Table 1) (in wt%). Mineralogical phase of CCG and CCG modified by $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (CCG-Zr) were determined by D8 Advance X-ray diffractometer (Germany, Bruker) and the results were presented (Figure 1).

Table 1. Chemical composition of fresh coal gangue (FCG) and calcinated coal gangue (CCG).

%	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	C
FCG	26.96	13.97	2.027	0.407	0.363	0.20	0.759	54.6
CCG	48.57	23.86	2.66	0.88	0.74	0.23	1.65	20.40

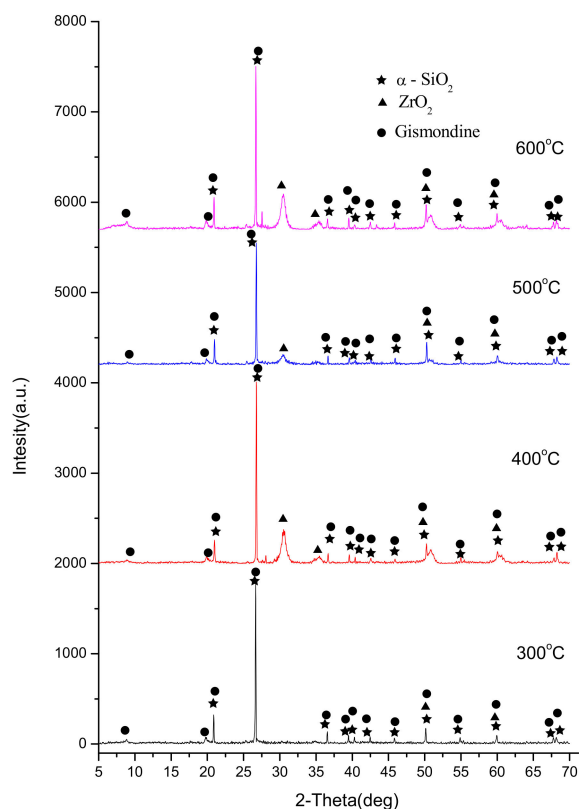


Figure 1. XRD patterns of coal gangue at different calcinated temperatures (300 °C, 400 °C, 500 °C, 600 °C).

In the experimental studies, the phosphate concentrations in the solutions were measured through a UV-VIS spectrophotometer (Hitachi U-2800) following an ascorbic acid method as stated in the standard methods [25]. Solution pH was determined with Sartorius PB 220 pH meter (Sartorius, Germany). The measurements were recorded in triplicate and the data were presented as the mean values at a 95% confidence interval.

2.4. Phosphate Removal Experiment

All the adsorption experiments were accomplished in batch mode of 150 mL conical flasks which were kept in shaker at 15 °C set at 180 rpm. A background electrolyte of 0.01 mol/L KCl was used to adjust ionic strength in all the batch experiments. The samples were centrifuged at 5000 r/min for 10 min and a clear supernatant aliquot was collected to analyze phosphate concentration. A stock solution (50 mg L⁻¹) of KH₂PO₄ was prepared by dissolving 0.2197 g in 1 L deionized water and dilutions of stock solution were administered in subsequent experiments. Phosphate concentrations from secondary effluents was simulated by diluting stock solution (50 mg L⁻¹) of KH₂PO₄ to 2 mg P/L.

2.4.1. Kinetic Experiments

For all experiments, the adsorbent (CCG-Zr) dose was 1 g placed into each reaction flask containing 50 mL of phosphate solution (2 mg P/L). The sampling time intervals were 10, 20, 40, 60, 80, 100 and 120 min. The operational conditions were: initial pH 2.5 under 15 °C and 180 rpm. There were 21 same samples for 7 time interval in the kinetic experiment and three samples were taken out for phosphate concentration analysis every time.

2.4.2. Effect of pH

To study the effect of pH, same adsorbent and adsorbate doses were used as for kinetics experiments. The effects of initial pH were investigated in the range of 2.5 to 11.5. The initial solution pH was adjusted by using either 0.1 M HCl or NaOH. All the flasks were capped to avoid evaporation and the pH values were analyzed after 2 h at 15 °C.

2.4.3. Effect of Dosage

Phosphate solution (2 mg P/L) was used for adsorption under varying doses of CCG-Zr (under initial pH 3.5, 15 °C, 180 rpm for 2 h). The CCG-Zr doses were in range of 1 to 60 g/L (1, 5, 10, 20, 40, and 60 g/L).

2.4.4. Isotherms Experiment

Isotherm experiments were conducted using 0.5 g of CCG-Zr into conical flasks containing 50 mL phosphate solutions. The initial phosphate concentrations ranged from 2.5 to 50 mg P/L (2.5, 5, 10, 20, 30, 40, and 50 mg P/L) at initial pH value of 3.5. The conical flasks were placed in the constant temperature shaker (15 °C and 180 rpm) for 120 min.

2.4.5. Regeneration of Adsorbent

The regeneration tests were carried out using CCG-Zr (50%) with 2 mg P/L of phosphate solution. After adsorption, the CCG-Zr (50%) was collected and used for desorption studies. Different concentrations of NaOH (0.1, 0.2, 0.3, 0.4, and 0.5 M) were utilized to test the possibility of CCG-Zr regeneration.

2.5. Data Processing

All the treatments and analysis were conducted in triplicate. Differences in the results were statistically analyzed using one-way ANOVA (S-N-K) test (SPSS 18.0) at $p < 0.05$.

3. Results and Discussion

3.1. Characterization of CCG-Zr

As shown in Table 1, Al₂O₃ content of calcinated coal gangue at 750 °C increased by 70.79%, while carbon content decreased by 62.64% compared with those in fresh coal gangue. The XRD patterns of CCG-Zr under different calcinated temperatures were illustrated in Figure 1, The major crystalline phase of CCG-Zr under different temperatures contained α -S₂O₂, Gismondine and ZrO₂. From Figure 1 it was evident that the peak assigned to quartz in these CCG-Zr was more intense which was attributed to its higher quartz content in these samples (Table 1). After exposure to different calcinated temperatures, several ZrO₂ characteristic peaks were evident at 30°, 35°, 50° and 60° in the XRD pattern of CCG-Zr (Figure 1) according to ICDD (International Centre for Diffraction Data) card No. 34-1084, 50-1089, and 37-1413. This observation verified the presence of ZrO₂ in CCG-Zr after the modification and calcination of ZrOCl₂·8H₂O. XRD of CCG-Zr at 300 °C only showed two weak peaks at 50° and 60°, respectively. It indicated that although ZrO₂ began to appear in an orthorhombic state [26], it was not well crystallized at 300 °C calcination which was supported by the low number and intensity of the orthorhombic ZrO₂ XRD peak in CCG-Zr at 300 °C. ZrO₂ mainly exists in tetrahedron crystalline or coexists in tetragonal and orthorhombic crystalline at 400, 500, and 600 °C [26].

3.2. Effect of Calcinated Temperature and ZrOCl₂·8H₂O/CCG Mass Ratio

Under experimental conditions (2 mg P/L, 20 g/L absorbent dose, and contact time of 2 h), all the calcinated coal gangue loaded with ZrOCl₂·8H₂O (ZrOCl₂·8H₂O/CCG (50%)) showed good performance regarding the phosphate removal with a phosphate removal efficiency of 88–93% while a

slight increase in calcinated temperatures resulted in significantly enhancing phosphate adsorption on the coal gangue-zirconia oxide composite material (Figure 2a) ($p < 0.05$). It was evident from Figure 1 that orthorhombic ZrO_2 at 300 °C turned into tetrahedral crystal or coexisted in tetrahedral and orthorhombic crystal at over 400 °C. Tetrahedral ZrO_2 crystal might have better affinities toward phosphate compared with orthorhombic ZrO_2 . Phosphate adsorption rapidly increased from 35% to 93% with an increasing Zr/CCG mass ratio from 0% up to 50%, indicative of enhanced phosphate adsorption caused by ZrO_2 addition. Further increasing that ratio from 50% to 100% only raised the phosphate removal efficiency by approximately 2% (Figure 2b) ($p < 0.05$). It might be due to fixed amount of adsorption sites in CCG which could not completely adsorb the excess dosage of Zr. Similar effects of lanthanum-doped mesoporous SiO_2 on the adsorption of phosphate have also been previously reported by Ou et al. [6]. Calcinated temperature (600 °C) and the $ZrOCl_2 \cdot 8H_2O$ /CCG mass ratio (50%) were chosen in the following phosphate adsorption experiments, considering both phosphate removal efficiencies and cost effectiveness.

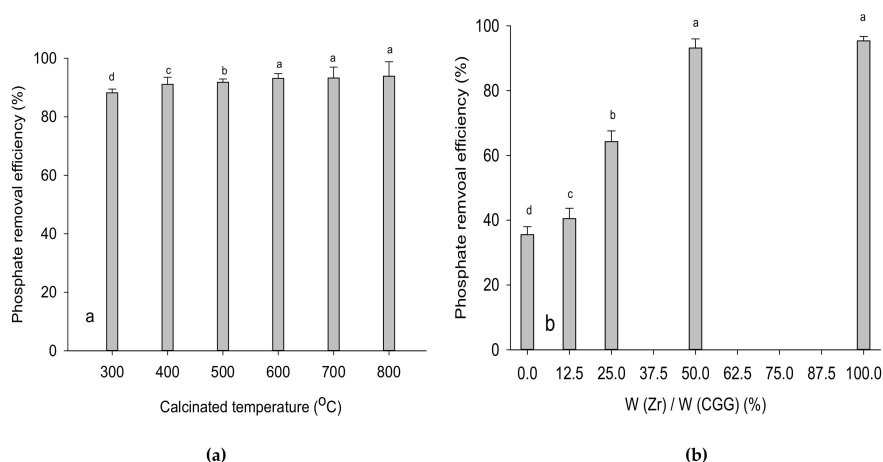


Figure 2. (a): Effect of different calcinated temperature (300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C) and (b): Effect of different $ZrOCl_2 \cdot 8H_2O$ /CCG mass ratio (0%, 12.5%, 25.0%, 50%, 100%) on phosphate removal efficiency on phosphate removal efficiency (calcinated time: 10 h, adsorbent: 20 g/L, particle size: 0.15 mm, temperature: 15 °C, stirring speed: 180 rpm, solution pH: 2.5, adsorptive time: 2 h). Different letters on the top of bars indicate significant differences between the treatments at $p < 0.05$ according to S-N-K tests.

3.3. Phosphate Adsorption Experiments

3.3.1. Effect of Contact Time

Phosphate adsorption rapidly increased during the startup of the experiment reaching at equilibrium within 20 min and then leveled off with further increase in contact time (Figure 3). At maximum adsorption, phosphate removal rate of 93% was attained from the solution. The large number, oxidation states and array of different functional groups on the activated coal gangue (e.g., Fe_2O_3 , Al_2O_3 , SiO_2 and zirconium oxide etc.) might be responsible for the high phosphate removal rate. Different types of adsorbent-adsorbate interactions may be involved in phosphate adsorption in current study, as reported by Liu et al. [19] and [20]. Apparently, CCG-Zr has potential application in the treatment of secondary effluents in terms of its strong adsorption for phosphate and high phosphate removal rate (Figure 3). Previously, Luo et al. [27] investigated phosphate adsorption onto $ZrOH$ through some modification by ammonium. The FTIR results confirmed the mechanism of phosphate adsorption on the inner sphere complexes and ligand exchange electrostatic interactions. Further modifications by dimethylamine improved phosphate adsorption from 22.9% to 33.9% as proved by XPS. It was recommended that zirconium hydroxide presented the excellent performances of anti-interference in real wastewater [27].

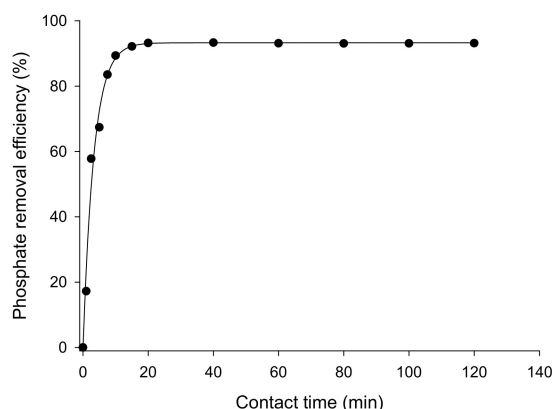


Figure 3. Effect of time on the efficiency of phosphate removal (initial phosphate concentration: 2.0 mg/L, adsorbent dose: 20 g/L, temperature: 15 °C, stirring speed: 180 rpm, pH: 2.5).

3.3.2. Effect of pH

Solution pH is an important variable that influences phosphate adsorption. Various phosphate species present in water include H_3PO_4 , H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} , and their relative chemical proportions depend on solution pH [28]. The CCG-Zr could adsorb phosphate over a wide pH range of 2.5–9.5 (Figure 4). The maximum phosphate removal rate (98%) was noted at pH 3.5, decreased with increasing pH, but still maintained around 72% at pH 9.5, even at low phosphate concentrations (2 mg/L). A decrease in phosphate adsorption on the CCG-Zr may be attributed to an increase in net negative charge on the adsorbent surface and phosphate ions and subsequent repulsion between the adsorbent and phosphate ions [19,27]. However, activated Al_2O_3 and CaO in the CCG-Zr could remove phosphate from solution by chemical co-precipitation and cation bridging at a higher pH [29]. Therefore, the CCG-Zr could maintain a high phosphate removal rate (>88%) from wastewater, even at pH 8.5.

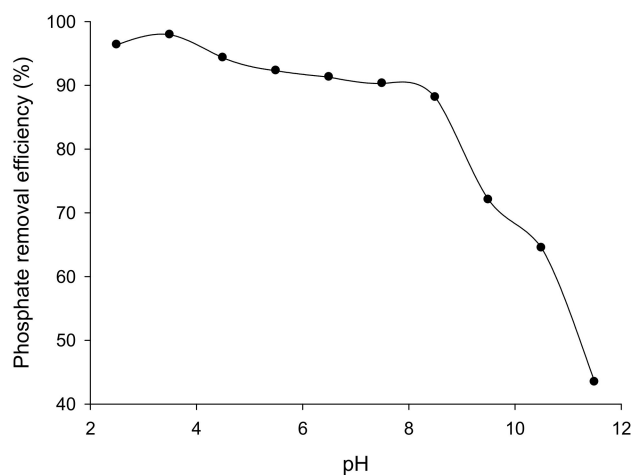


Figure 4. Effect of pH on the efficiency of phosphate removal (initial phosphate concentration: 2.0 mg/L, adsorbent dose: 20 g/L, temperature: 15 °C, stirring speed: 180 rpm, time: 20 min).

3.3.3. Effect of Adsorbent Dose

Phosphate removal rates generally had linear relationship with the adsorbent dose i.e. increased with increasing adsorbent dose and reached at the maximum (98%) for CCG-Zr dosage of 20 g/L (Figure 5). Phosphate removal rate tended to decrease with further increase in CCG-Zr dosage, but leveled off at 91% when adsorbent dosage was 60 g/L. A slight decrease in phosphate removal rate at higher adsorbent dosage may result from different phosphate sorption mechanisms involved in the

phosphate removal process, adsorption being dominant at low dosages but precipitation at the higher adsorbent dosage.

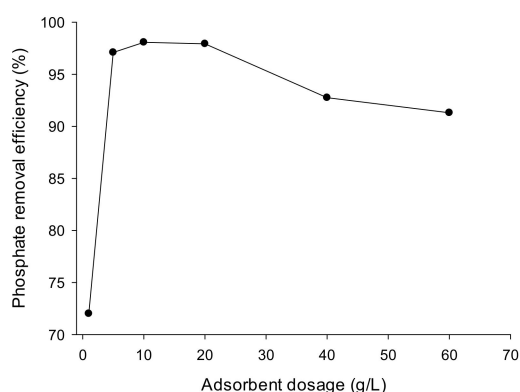


Figure 5. Effect of adsorbent dosage on phosphate removal by CCG-Zr (initial phosphate concentration: 2.0 mg/L, pH: 3.5, temperature: 15 °C, stirring speed: 180 rpm, time: 20 min).

3.3.4. Effect of Phosphate Concentration

The Langmuir and Freundlich models are often used to describe sorption isotherms of phosphate in wastewaters [5]. A linear form of the Langmuir and Freundlich equation [30] is expressed as:

$$1/q_e = 1/q_m b c_e + 1/q_m \quad (1)$$

$$\lg q_e = 1/n \lg c_e + \lg K_F \quad (2)$$

where q_e is the amount of phosphate adsorbed at equilibrium (mg/kg), c_e is phosphate concentration at equilibrium (mg/L), q_m is maximum adsorption of phosphate (mg/kg), and b is a constant related to phosphate binding energy on adsorbent (L/kg). K_F and n are constants related to adsorption characteristics in the Freundlich model.

The experimental data fitted well to the Langmuir and Freundlich equations, with correlation coefficients ranging from 0.96 to 0.97. The estimated values of phosphate adsorption parameters obtained from these models were shown in Table 2. A high value ($n > 1$) indicated favorable adsorption. The calculated maximum adsorption capacity was 8.55 mg/g which is larger than that of amorphous zirconium hydroxide (2.5 mg P/g) [31], La doped vesuvianite (6.7 mg P/g) [32], or MgMn layered double hydroxides (7.3 mg P/g) [33].

Table 2. Estimated isotherm parameters for phosphate adsorption on CCG-Zr.

Adsorption Isotherms	Linear Forms	Equation of Linear Regression	Parameters and Correlation Coefficient
Langmuir	$1/q_e = 1/(bq_m C_e) + 1/q_m$	$1/q_e = 1/(bq_m C_e) + 0.5906$	$R^2 = 0.9674$
Freundlich	$\ln q_e = 1/n \ln C_e + \ln K_F$	$\ln q_e = 0.3188 \ln C_e + 0.027$	$R^2 = 0.9747$

The experimental data fitted better with the Freundlich ($R^2 = 0.9747$) than Langmuir model ($R^2 = 0.9674$), since the Freundlich equation assumes that the surface adsorption involves multilayer reactions. Besides adsorption; Al, Fe, Ca ions or oxides and some other components of CCG-Zr may also contribute to phosphate removal by precipitation to a certain extent.

3.3.5. Regeneration of Adsorbent

Regeneration of CCG-Zr is crucial for its economical application. NaOH was used to regenerate phosphate adsorbed on CCG-Zr (Figure 6) ($p < 0.05$). When the alkalinity reached 0.4 M, the maximum

regeneration efficiency of 80% was achieved. The results indicated that this CCG-Zr could be regenerated and had a great potential to be used as an adsorbent for phosphate removal from secondary effluents.

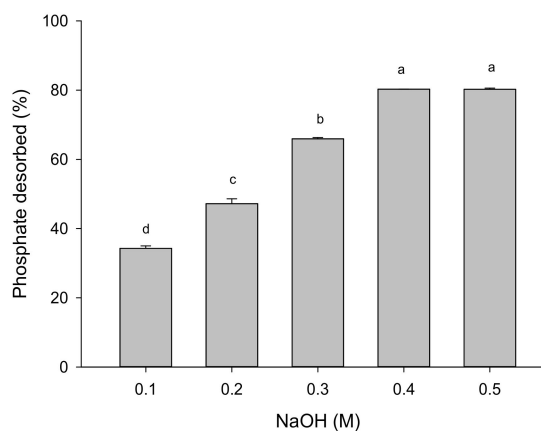


Figure 6. Desorption of phosphate from CCG-Zr (50%) using different concentrations of NaOH solution (adsorbent dose: 20 g/L, stirring speed: 180 rpm, Temperature: 15 °C, time: 2 h). Different letters on the top of bars indicate significant differences between the treatments at $p < 0.05$ according to S-N-K tests.

4. Conclusions

This study indicated that the newly developed CCG-Zr had higher phosphate removal efficiencies compared with calcinated coal gangue. CCG-Zr could reach equilibrium phosphate removal rate for 2 mg/L of initial phosphate concentration within 20 min. The CCG-Zr has a high removal rate of phosphate at low concentrations (2 mg/L) over a wide pH range. The adsorption isotherms fitted better to the Freundlich model than to the Langmuir model. The maximum phosphate adsorption capacity of the CCG-Zr was 8.55 mg/g. It was demonstrated that 80% of the phosphate could be desorbed by using NaOH. These results suggested that the CCG-Zr could be potentially applied for phosphate removal from secondary effluents.

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Conflicts of Interest: The authors declare no conflict of interest.

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