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Phosphorus removal from domestic sewage by adsorption combined photocatalytic reduction with red mud

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ABSTRACT

Phosphorus removal from domestic sewage by adsorption combined photocatalytic reduction with raw and modified red mud (RM) was studied in this paper. The results indicated that RM dosage, reaction time, stirring rate, phosphorus concentration, and initial pH of solution (pH_i) were the main factors to effect on phosphorus removal. It was found that the phosphorus removal efficiency of modified red mud (RM-m) under the photocatalytic test conditions was higher than only by adsorption process, while raw red mud (RM-raw) showed no significant difference under the two conditions. With initial phosphorus concentration 8.26 mg/L, reaction time 60 min, stirring rate 200 r/min, under the adsorption and photocatalytic test conditions, the optimum dosage and pH_i of both RM-raw and RM-m were 1.8 g/L and 4.0, respectively, and the corresponding phosphorus removal of RM-raw and RM-m were 90.18 and 91.70%, respectively. The optimum amount of RM-m under the two conditions were 1.6 and 1.5 g/L, respectively, the optimal pH_i 3.0, correspondingly, the phosphorus removal could reach high up to 94.30 and 99.96%, respectively.

Keywords: Adsorption; Domestic sewage; Modification; Photocatalytic reduction; Phosphorus removal; Red mud

1. Introduction

Excess phosphorus present in wastewater is one of the main causes of eutrophication. The current wastewater treatment technologies include physical–chemical methods, photochemical methods, and biological methods [1–3]. Among them, despite the high removal of the total phosphorus, the enhanced biological treatment is highly variable due to operational difficulties [4]. Although photochemical methods have been widely used for wastewater treatment [5], phosphorus removal by photochemical methods has rarely been reported. Great attention has been paid to physical–chemical methods, which mainly include adsorption, coagulation, crystallization, electrodialysis, reverse

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osmosis, etc. [6]. Chemicals such as iron and aluminum salt, calcium compounds, and ferric chloride are the common precipitants used for phosphorus removal, but cost and sludge productions limited the further application in wastewater treatment [7,8]. Nowadays, adsorption process has become a dominant process because of its advantages including adsorbent recycling, high adsorption capacity, and low cost.

The adsorbents widely used contain natural material and waste residue as well as its modified material, porous material, and synthetic adsorbent [9–12]. Previous studies have shown that the adsorption capacity of the phosphorus exists in many low-cost sorbents, such as fly ash [13], bentonite, natural zeolite, alum sludge [14], red mud [15–18], and other waste materials [19]. Red mud (RM) is a waste residue formed after the caustic digestion of bauxite during the production of alumina. It has been studied as a coagulant for removal of pollutants, such as AsO_4^{3-} [20], H_2S [21], NO_3^- [22], PO_4^{3-}, Cu^{2+} [23], Zn^{2+}, Ni^{2+}, and CrO_4^{2-} [24] from aqueous solution, for it is mainly composed of fine-grained particles containing aluminum oxide, iron oxide, silica, titanium oxides, and hydroxides. RM is unsuitable for direct application due to the high dosage, alkalinity, and low efficiency, although it was found to be good phosphorus-removing medium.

In recent years, development in using RM as adsorbents for gas cleaning and wastewater treatment as well as catalysts for waste gas and liquid cleaning has also been widely reported [25]. In the paper, modified RM with a small amount of fine-grained semiconductors was chosen as absorbent and photocatalyst, and the phosphorus removal from domestic sewage by adsorption combined photocatalytic reduction was firstly studied, aiming to offer a new research direction for advanced treatment of phosphorus in wastewater.

2. Materials and methods

2.1. Materials

The domestic sewage tested in the experiment was taken from a living district in Wuhan, Hubei province, China. The pH value, phosphorus concentration, and turbidity were 7.0, 8.3 mg/L and 65 NTU, respectively.

The RM-raw was obtained from Shandong Aluminum Industry Corporation, Shandong province, China. The particle size was averaged 20 mesh. The preparation of the RM-m was briefly described as follows: firstly, the RM-raw was washed and air dried, then pretreated at 600°C for 2 h and transferred into the glass reactor with HCl (the concentration was 0.5–0.8 mol/L) at 50–60 g(RM-raw)/L(HCl) stirring for 1 h. Then, the suspended liquids were fully precipitated, and the prepared products were washed, dried, and sieved through a 100 mesh sieve, sealed, and preserved.

2.2. Experiments

2.2.1. Adsorption test

Domestic sewage and dephosphorization agents (RM-raw and RM-m) (0–2.5 g/L) were put into the reactor and stirred for some time (5–90 min) with the certain stirring rate (50–350 r/min) at 25°C. The phosphorus concentration and pH value of supernatant was measured after settling for 4 h.

2.2.2. Photocatalytic test

The testing apparatus is shown in Fig. 1. It consists of a glass vessel, a magnetic stirring apparatus, a nitrogen pump, and a 125 W high-pressure mercury lamp (GYZ 220-125W, JingShuo lighting company, China). The effective range of the light spectrum was between 350 and 450 nm, with the main peak 365 nm, and the luminous flux 1,500 Lm. The lamp which mainly emitted a visible light was used as a light source of the photocatalytic reduction.

Domestic sewage and dephosphorization agents (RM-raw and RM-m) (0–2.5 g/L) were put into the reactor, and the suspension was constantly stirred for some time (5–90 min) with certain stirring rate (50–350 r/min) at 25°C under continuous stream of nitrogen with a velocity of 0.1 L/min during the reaction. The visible light from the high-pressure mercury lamp (125 W) irradiated perpendicularly to the solution and the distance between the lamp and the liquid level was 30 cm. At given irradiation time intervals (5, 15, 30, 45, 60, and 90 min), liquid samples were taken from the suspension and settled for 4 h, and then, the phosphorus in the supernatant was measured.

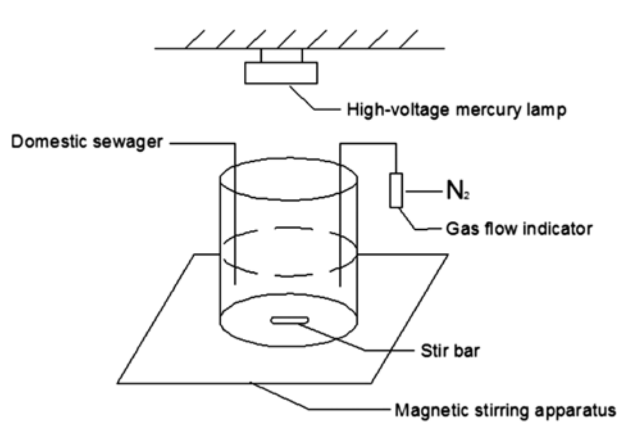

Fig. 1. Sketch of photocatalytic reactor.

2.3. Analytical methods

The phosphorus was measured using the ammonium molybdate spectrophotometric method with UV–Visible spectrophotometer (DR4000/U, HACH company, USA). A pH meter (PHS-3C, Shanghai Leici instrument plant, China) was used to measure the pH of the solution. The micrograph of the dephosphorization agent was observed using an analytical transmission electron microscope (H-600 STEM/EDX PV9100, HITACHI, Japan). The specific surface area (SBET) of RM was determined by the BET nitrogen gas sorption method using a full automaticity specific surface area analyzer (Gemini2360, Micromeritics, USA). The composition of RM was measured with the full spectrum of direct reading inductively coupled plasma emission spectrometer (Optima 4300DV, Perkin Elmer Ltd., USA).

All the chemicals and reagents used in this study were of analytical grade. All glassware and sample bottles were soaked in diluted HCl solution for 12 h, then washed and rinsed three times with deionized water. Deionized water was also used for the preparation of solutions. All experiments were conducted in duplicate and the average values were used for data analysis. Each water quality was tested according to *Water and Wastewater Monitoring and Analysis Methods* (fourth ed., Chinese).

3. Results and discussion

3.1. The characteristics of RM

The composition and property of RM-raw and RM-m are given in Table 1. From the table, it could be found that the composition of the RM-m was different from the raw sample. The main compositions were turned to ferric hydroxide and aluminum hydroxides, and some soluble salts were removed (Fig. 2). Besides, the alkalinity of RM was reduced after modification treatment; The BET surface area of the RM-m indicated that the surface area was increased, the moisture in the RM-raw was reduced and the interior pores were dredged in the modification process. Scanning electron microscope (SEM) pictures are listed in Fig. 3. As shown in Fig. 3, both the RM-raw and RM-m contained various particles with different size and shape. RM-m was a very fine material in terms of particle size distribution, having an average particle size <500 nm, and some particles were even smaller than 50 nm, while the average particle size of RM-raw was much larger. Some crystals could be found in the RM-m, and in addition, the RM-m also presented porous surface.

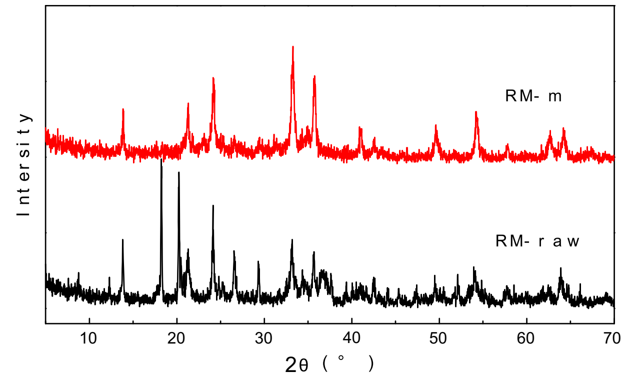

Fig. 2. XRD patterns of RM-raw and RM-m.

3.2. The factors affected phosphorus removal

Much preliminary work has been done to optimize the experimental conditions. The result of the batch adsorption test indicated that the main factors effecting on the removal of phosphorus from the domestic sewage were the dosage of dephosphorization agent, stirring rate, reaction time, pH_i and phosphorus concentration, and so on. The results of photocatalytic test indicated that the phosphorus in the domestic sewage could not be photodegradated only by irradiation with high-pressure mercury lamp.

3.2.1. Effect of RM dosage

The effect of RM dosage on the removing of phosphorus from aqueous solution is shown in Fig. 4 ($pH_i = 7$, reaction time was 60 min and stirring rate was 200 r/min). It showed that the phosphorus removal efficiency increased with increasing the dosage of RM for a given initial pH. From Fig. 4, it was indicated that both of the optimum dosage of RM-raw under the above-mentioned adsorption and photocatalytic conditions was 1.8 g/L, the corresponding phosphorus removal were 90.18 and 91.70%, respectively. The phosphorus removal efficiency was not improved remarkably for RM-raw under the photocatalytic conditions.

Table 1
Composition and property of RM-raw and RM-m (wt.%)

	Na_2O	Al_2O_3	SiO_2	CaO	TiO_2	Fe_2O_3	MgO	ZnO	pH	SBET ($m^2 g^{-1}$)
RM-raw	15.06	25.96	23.23	2.39	3.52	28.69	0.16	0.63	10.19	14.76
RM-m	10.12	28.23	23.87	1.93	4.35	30.35	0.11	0.41	7.38	19.22

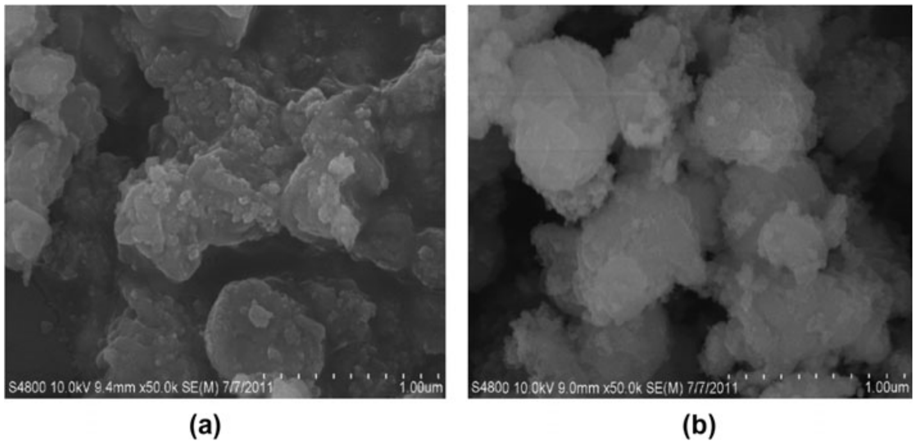

Fig. 3. SEM photographs of RM-raw and RM-m (a: RM-raw, b: RM-m).

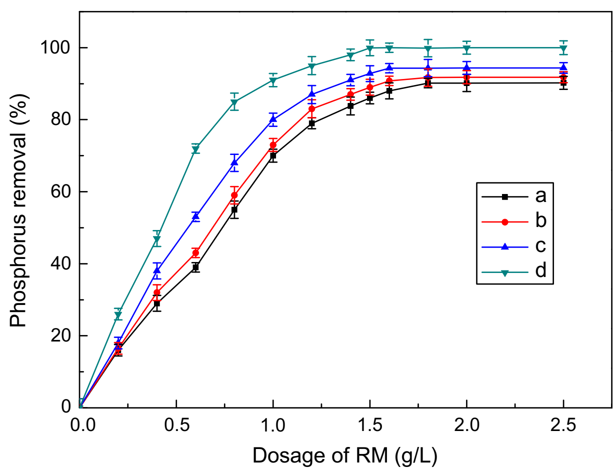

Fig. 4. Effect of RM dosage on the phosphorus removal (a: RM-raw under the adsorption test conditions; b: RM-raw under the photocatalytic test conditions; c: RM-m under the adsorption test conditions; d: RM-m under the photocatalytic test conditions).

For the RM-m under the adsorption test conditions, the phosphorus removal reached 94.30% when the dosage of RM-m was 1.6 g/L. And, for the RM-m under the photocatalytic test conditions, the phosphorus in the solution was almost undetectable when the dosage of RM-m was more than 1.5 g/L. It could be seen that the phosphorus removal efficiency of RM-m under the irradiation was much higher than RM-m only under the adsorption test conditions without irradiation.

The potential reason for the higher removal efficiency was that in the process of modification, the particle size of RM became smaller, the content of TiO_2 in the RM was increased, and the iron oxide and other metal compounds in the RM-m mixed with fine-grained TiO_2 particles served as TiO_2 modifiers. The metal-doped TiO_2 might extend the range of adsorption to light and improved the capability to visible light, so the photocatalytic activities of the small amounts of TiO_2 in RM-m were enhanced. Thus, in the photocatalytic test conditions, RM-m was not only performed as adsorbent, but also may have acted as photocatalyst. The reduction product of phosphorus (may be phosphine) in the processes of photocatalytic could not be detected due to the little quantity, while parts of the phosphorus escaped from the solution in gaseous form has been verified by the mass conservation of phosphorus. And, the specific reaction process need to be further explored.

3.2.2. Effect of the pH

Huang et al. [26] and Yue et al. [27] have demonstrated that pH_i had a great influence on the removal of phosphorus from aqueous solution. The effect of pH_i on the removal of phosphorus was observed by adjusting pH of the solution using 1 mol/L HC1 or 1 mol/L NaOH. The phosphorus removal by the dephosphorization agents (RM-raw and RM-m) is shown in Fig. 5 when pH_i was 1, 3, 4, 5, 7, 9, and 11 (the dosage of RM was 1.8 g/L, reaction time was 60 min and stirring rate was 200 r/min), and the final pH (pH_f) of the solution is also determined (Fig. 6). The phosphorus removal of RM-raw reached maximum at pH_i 3, then the removal rate was decreased with the increase of pH_i. For the RM-m, the optimal pH_i was 4 under the adsorption test conditions as well as the photocatalytic test conditions, and showed the similar trend as RM-raw. As seen from Fig. 6, pH_f of the solution was increased in varying degrees with increasing the pH_i.

The effect of pH on the phosphorus removing might be explained by the change of orthophosphorus compounds with pH. In the medium of strong acid,

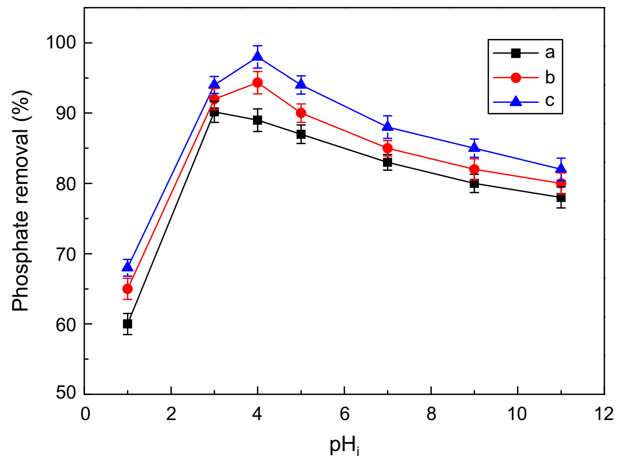

Fig. 5. Effect of initial pH on phosphorus removal (a: RM-raw under the adsorption test conditions; b: RM-m under the adsorption test conditions; c: RM-m under the photocatalytic test conditions).

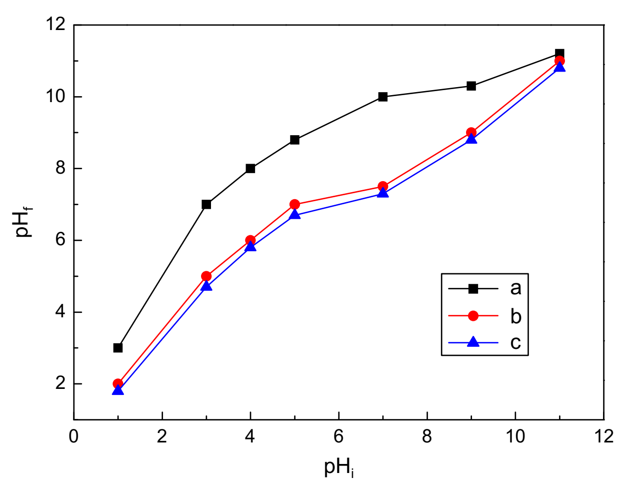

Fig. 6. pH of solution after the reaction (a: RM-raw under the adsorption test conditions; b: RM-m under the adsorption test conditions; c: RM-m under the photocatalytic test conditions).

the main form of phosphorus is H_3PO_4, which may not easily be adsorbed by RM. In the alkaline solution, phosphorus removal was gradually reduced partly because the main form PO_4^{3-} would be completed by OH^- on the surface of RM, and the similar trend was reported [28]. $H_2PO_4^-$ and HPO_4^{2-} are the predominant aqueous species in aqueous media near neutral pH range, and such forms of phosphorus were most likely to be adsorbed by RM. The best treatment results of RM-raw and RM-m were gained when the pH$_f$ were slightly acid.

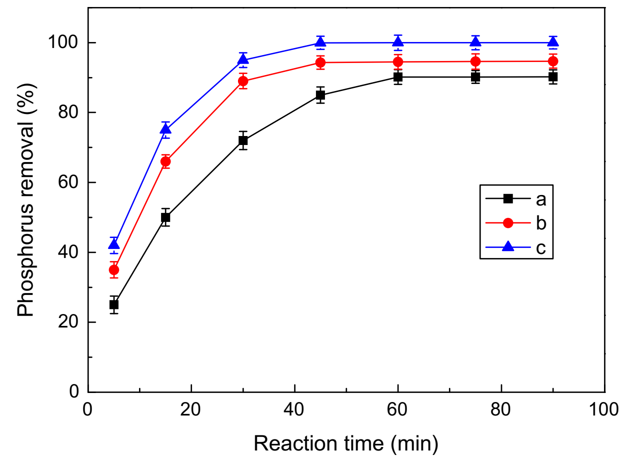

Fig. 7. Effect of reaction time on the phosphorus removal (a: RM-raw under the adsorption test conditions; b: RM-m under the adsorption test conditions; c: RM-m under the photocatalytic test conditions).

3.2.3. Effect of reaction time

The result of the effect of reaction time on the phosphorus removal is shown in Fig. 7 (the dosage of RM was 1.8 g/L, pH$_i$ = 7, and stirring rate was 200 r/min). After the initial rapid reaction, phosphorus removal of the RM-raw and RM-m kept steadily. As seen from Fig. 7, the RM-raw and RM-m had the similar phosphate removing trends, and the peak value was achieved at 60 min for RM-raw under the adsorption test conditions and at 45 min for RM-m under the adsorption as well as photocatalytic test conditions.

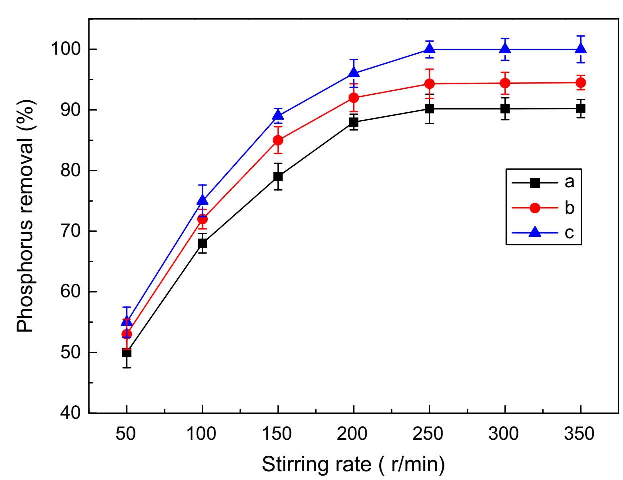

Fig. 8. Effect of stirring rate on the phosphorus removal (a: RM-raw under the adsorption test conditions; b: RM-m under the adsorption test conditions; c: RM-m under the photocatalytic test conditions).

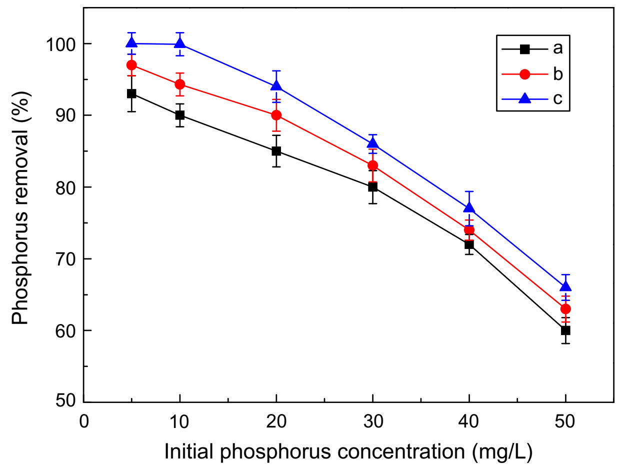

Fig. 9. Effect of initial phosphorus concentration on the phosphorus removal (a: RM-raw under the adsorption test conditions; b: RM-m under the adsorption test conditions; c: RM-m under the photocatalytic test conditions).

3.2.4. Effect of stirring rate

The result of phosphorus removal by RM-raw and RM-m under the adsorption and photocatalytic test conditions is shown in Fig. 8 when stirring rate was 50, 100, 150, 200, 250, 300, and 350 r/min (the dosage of RM was 1.8 g/L, $pH_i = 7$, and reaction time was 60 min). The phosphorus removal of RM-raw under the adsorption test conditions and RM-m under the adsorption and photocatalytic test conditions reached maximum at 200 r/min, and then the removal rate become smooth and approached a limiting value.

3.2.5. Effect of initial phosphorus concentration

The phosphorus removal efficiency of RM-raw and RM-m as a function of phosphorus concentration is shown in Fig. 9. RM-raw and RM-m under the adsorption or photocatalytic test conditions have the similar phosphorus removal tendency, the removal efficiency decreased with increasing initial phosphorus concentration for a given dosage of RM. For the RM-m under the photocatalytic test conditions, the phosphorus in the solution was almost undetectable (<0.01 mg/L) when the initial phosphorus concentration was lower than 10 mg/L. It is thus clear that the method of adsorption combined photocatalytic reduction with RM-m was successful in removing phosphorus from domestic sewage, simple in operating, and low in cost.

4. Conclusions

Based on the results of the experiments introduced above, some conclusions are drawn as follows:

(1) The main compositions of RM after modification process were turned to ferric hydroxide and aluminum hydroxide, the alkalinity reduced and the BET surface area increased. The average particle size was less than 500 nm.

(2) RM dosage, reaction time, stirring rate, phosphorus concentration, and initial pH of solution (pH_i) were the main factors effect on phosphorus removal.

(3) The phosphorus removal of RM-m under the photocatalytic test conditions was higher than that without the illumination, and it could reach high up to 99.96% with optimum reaction conditions (the dosage of RM-m was 1.5 g/L, $pH_i = 4$, reaction time was 60 min and stirring rate was 200 r/min), while the phosphorus removal of RM-raw showed no great difference under the two conditions.

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