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Simultaneous phosphate and COD_{cr} removals for landfill leachate using modified honeycomb cinders as an adsorbent

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ABSTRACT

In this study, honeycomb cinders were employed to remove phosphate and Chemical Oxygen Demand (COD_{cr}) simultaneously for landfill leachate treatment. Operating conditions of honeycomb cinders pretreatment, pH, temperature, honeycomb cinders dosage, reaction time, and settling time, were evaluated and optimized. The results revealed that the removal efficiencies of both phosphate and COD_{cr} could be increased up to 99.9% and 66.7% under the optimal conditions, respectively. Moreover, the structures of raw/modified honeycomb cinders and resulting precipitates were detected by Scanning Electron Microscope (SEM), Energy Dispersive Spectrometers (EDS) analysis and X-ray Diffraction (XRD). The results suggested that the adsorption method using honeycomb cinders might be an effective strategy as a pretreatment technology for landfill leachate treatment.

1. Introduction

Landfill leachate, generated by excess rainwater and moisture percolating through the waste layers of sanitary landfill site, is generally featured in China by deep color, strong stench, large amounts of NH_4^+–N, high strength of COD_{cr} with much lower biodegradability, rich of heavy metals and recalcitrant compounds. Since the inadequate municipal waste solid collection system employed in many cities resulted in the waste solids full of organic and hazardous material, the treatment of landfill leachate is considered to be very difficult. Up to now, there is lacking of a recommended technology for landfill leachate treatment in China.

At present, some technologies used in practice can be summarized as physical, chemical and biological methods, such as adsorption [1], chemical precipitation [2], biological treatment [3–5], membrane treatment [6], and advanced oxidation processes [7–11]. In particular, adsorption as a surface phenomenon, operated by a fluid mixture of multi-components absorbed to the surface of a solid adsorbent *via* physical or chemical styles, is believed to be one of the most efficient and promising approaches for landfill leachate treatment [12], with the merits of lower energy consumption and higher treatment efficiency. And in the adsorption technologies, the adsorbents are considered to be crucial factors, among which activated carbon, [13,14], coal fly ash [15], pine bark and blast furnace slag [16] are normally used.

The honeycomb cinders as the products of honeycomb briquette combustion are mainly made of silicon dioxide, aluminium oxide, ferric oxide and calcium oxide. With the characteristic of large specific surface areas, the honeycomb cinders are generally employed to make the air clean, protect against moisture. It can also be used as paving material and basin land for growing flowers. Investigations have shown that the modified honeycomb cinders could be used to greatly adsorb nitrophenol and methylene blue. However, to our knowledge, employing honeycomb cinder as adsorbent to treat landfill leachate have not yet been achieved.

In the present work, the honeycomb cinders were employed to treat landfill leachate. After acidification pretreatment, the specific surface areas of honeycomb cinders can largely increase its adsorption ability. Under optimal conditions of pH, temperature, honeycomb cinders dose, reaction time and settling time, the removal efficiencies of COD_{cr} and phosphate could be substantially improved. Furthermore, the structures and characteristics of raw/modified honeycomb cinders and resulting precipitates were

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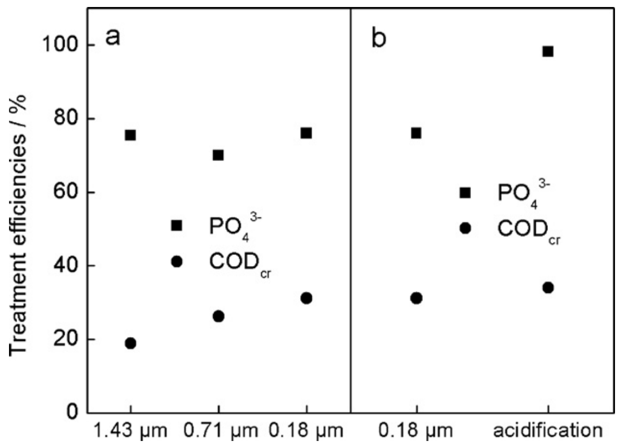

Fig. 1. COD_{cr} and PO_4^{3-} removal efficiencies by employing honeycomb cinders with particle sizes of 0.71–1.43 μm (A), 0.18–0.71 μm (B), less than 0.18 μm (C). Less than 0.18 μm (D) after acidified. Experimental conditions: pH of 8.8, temperature of 30 °C, honeycomb cinders dose of 10.0 g L^{-1}, reaction time of 20 min and settling time of 20 min (the conditions of this experiment were selected on the basis of previous experiments).

probed by Scanning Electron Microscope (SEM), Energy Dispersive Spectrometers (EDS) analysis and X-ray Diffraction (XRD). The aim of this study was to present an effective strategy as a pretreatment technology for landfill leachate.

2. Materials and methods

2.1. Materials

The raw landfill leachate, obtained from the Hei Mi-Feng landfill (Changsha, China), was collected from the buffer pond and was stored at 4 °C in a 20 L plastic container. In this research, the landfill leachate was pretreated by struvite precipitation. The detailed parameters were detected as follows: color 20 ± 5.00%, pH 8.8 ± 1.13%, TS 2712 ± 1.05%, NH_4^+–N 2.27 ± 2.68%, PO_4^{3-} 77 ± 3.44%, COD_{cr} 6666 ± 4.40%, Mg^{2+} 45 ± 3.85%, Ca^{2+} 140 ± 2.58%, K^+ 2715 ± 1.33%, Na^+ 7065 ± 1.59%, HCO_3^{2-} 146 ± 3.81%, CO_3^{2-} 14 ± 3.27%.

Dried raw honeycomb cinders are brown color, obtained from a local restaurant in Changsha. And then were washed by distilled water for 3 times and dried in a drying closet for 24 h at 105 °C for using.

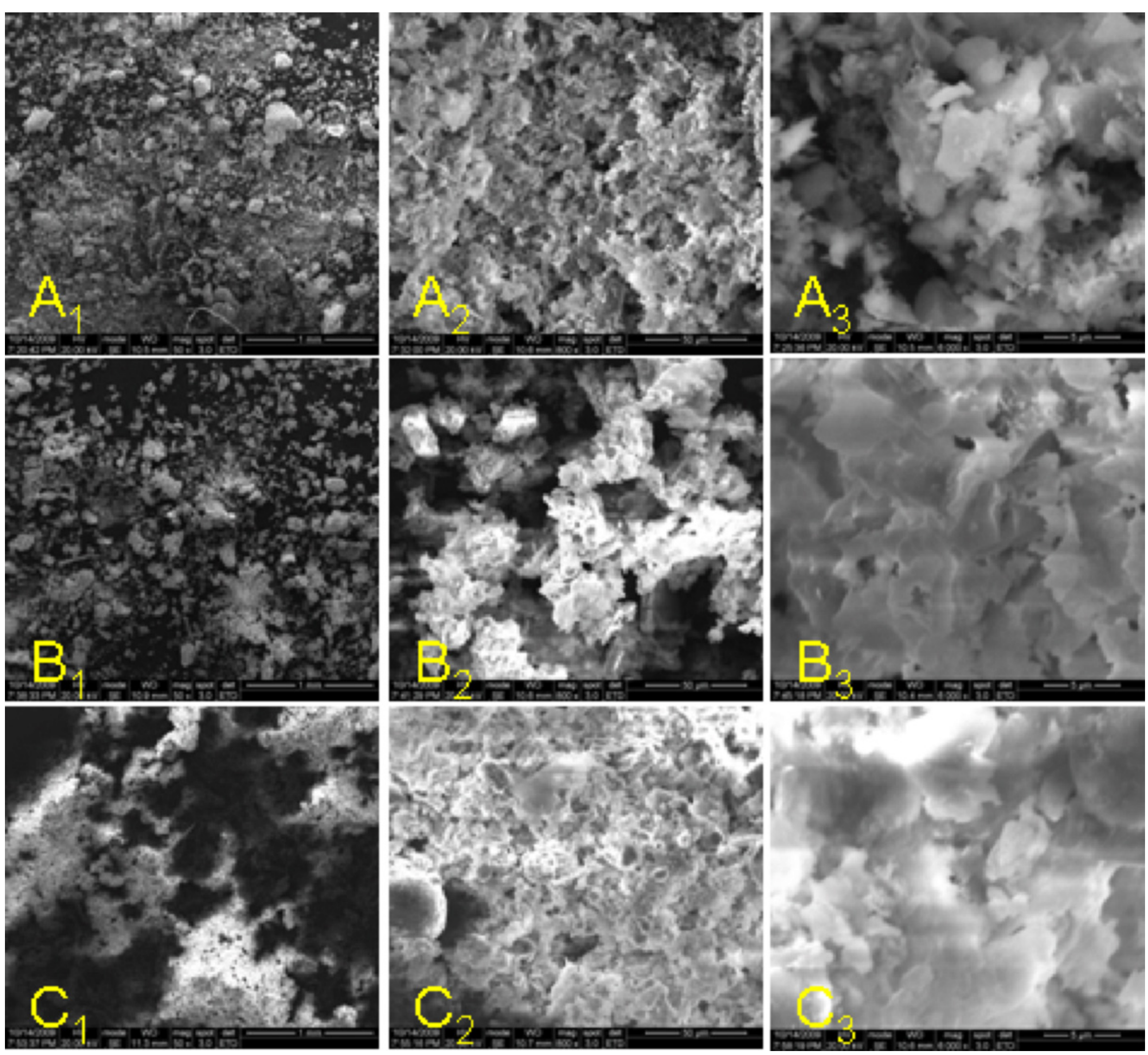

Fig. 2. SEM images of raw (A_1–A_3) and modified (B_1–B_3) honeycomb cinders with various resolutions of 1 mm, 50 μm, 5 μm, and of the resulting precipitates (C_1–C_3).

2.2. Experimental procedures

The experiments were carried out in batch model. A desired amount of the honeycomb cinders were added to 100.0 mL samples which were heated in water bath under controlled temperature. The desired pH was adjusted with diluted HCl or NaOH solution. The samples were stirred by magnetic stirrers. After the desired reaction and settling times, the samples were filtered by qualitative filter papers to detect phosphate and COD_{cr}. The raw/acidified honeycomb cinders and resulting precipitates were dried at 30 °C for 48 h for SEM, EDS, and XRD analysis. Repeated experiments were carried out, and the results were obtained in triplicate within (±5%) data deviation.

2.3. Analytical methods

The temperature of samples was controlled by water bath (DK-98-1, Tianjin taisite instrument Co., Ltd, China). pH was recorded by pH meter (pH330i, WTW, Germany). The color, TS, NH_4^+–N, CO_3^{2-}, HCO_3^- and PO_4^{3-} were measured by spectrophotometer according to APHA Standard Methods [17]. COD_{cr} was measured by modle MS-3 microware digestion system (South China institute of environment sciences, MEP, China). Mg^{2+}, Ca^{2+}, K^+ and Na^+ were measured by novAA 300 FAAS Determination (Jena, Germany). Raw/modified honeycomb cinders and resulting precipitates were investigated by means of SEM (Quanta 200, FEI, Germany) and XRD (D-5000, Siemens, Germany). Removal efficiencies of treatment were obtained using the following formula: removal (%) = $[(C_i–C_f)/C_i] \times 100$, where C_i and C_f are the initial and post-treated concentration of PO_4^{3-} and COD_{cr}, respectively.

3. Results and discussion

3.1. Pretreatment for honeycomb cinders

3.1.1. Particle sizes of honeycomb cinders

To investigate the effect of particle sizes on treatment efficiencies, honeycomb cinders were sieved for three kinds of particle size distribution including 0.71–1.43 μm, 0.18–0.71 μm, and less than 0.18 μm. Fig. 1a shows that the highest removal efficiencies of both PO_4^{3-} and COD_{cr} were obtained at 76.0% and 31.1%, respectively, when the particle size of honeycomb cinders was smaller than 0.18 μm. Accompanied with the increase of particle sizes, the removal efficiencies went down obviously, probably due to smaller surface area of larger particles or external mass transfer limitations. Therefore, less than 0.18 μm was considered to be the optimal particle size of honeycomb cinders in this experiment.

3.1.2. Raw/modified honeycomb cinders

Fig. 1b shows that 34.0% COD_{cr} and 98.2% PO_4^{3-} removal efficiencies with modified honeycomb cinders were higher than that of raw honeycomb cinders. Compared with the raw honeycomb cinders (Fig. 2A_1–A_3), the structures of modified honeycomb cinders were changed to tabular crystal and had a bigger surface area, which were believed to be more effective for pollutants removals. Moreover, acidified honeycomb cinders could be dissolved at pH of 8.8. Table 1 lists the contents of elements such as C, O, Na, and S in modified honeycomb cinders, which were found to be smaller than that of raw honeycomb cinders. The analysis of XRD (Fig. 3a and b) indicates that the compositions of modified honeycomb cinders were less than that of raw honeycomb cinders. It would be concluded that the modified honeycomb cinders had a better performance for the removals of pollutants in landfill leachate than the raw one.

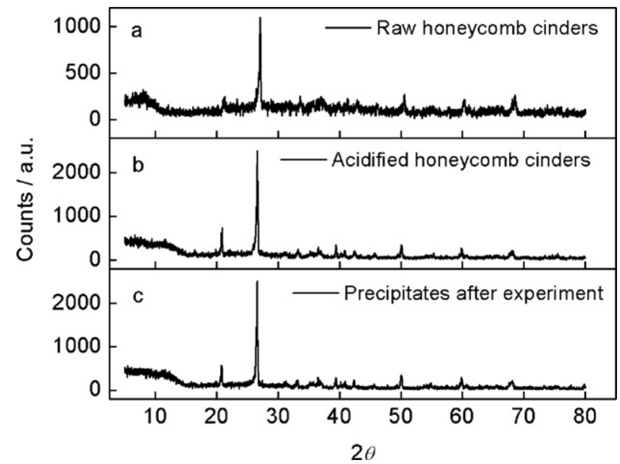

Fig. 3. XRD analysis of raw (a) and modified (b) honeycomb cinders, and resulting precipitates (c).

3.2. Optimal pH

Fig. 4 demonstrates that the highest treatment efficiencies were obtained at pH 5.0, which reached to 100% of PO_4^{3-} and 53.2% of COD_{cr} removals. When pH was 2.0 or lower than 2.0, protonation of Fe in honeycomb cinders occurred. When pH was increased from 2.0 to 3.0, Fe^{3+} was gradually precipitated by the form of $Fe(OH)_3$. And when pH was higher than 3.0, Fe^{3+} was completely precipitated by the form of $Fe(OH)_3$. Moreover, When pH was 5.0 or lower than 5.0, protonation of Al in honeycomb cinders occurred. When pH was increased from 5.0 to 6.0, Al^{3+} was gradually precipitated by the form of $Al(OH)_3$. When pH was ranged between 5.0 and 13.0, Al^{3+} was completely precipitated by the form of $Al(OH)_3$. In this experiment, when pH was 2.0, the pollutants removals might be solely relied on physical adsorption. When pH was enhanced from 2.0 to 5.0, the efficiency of COD_{cr} removal was maintained at 49.0–53.2%, while the efficiency of PO_4^{3-} removal was slightly increased from 92.3% to 100%. When pH was 5.0, the pollutants removals might be relied not only on physical adsorption, but also on chemical flocculation attributed by $Al(OH)_3$ and $Fe(OH)_3$. However, when pH was higher than 5.0, both COD_{cr} and PO_4^{3-} removal efficiencies were decreased. Therefore, pH of 5.0 was chosen as the optimal pH.

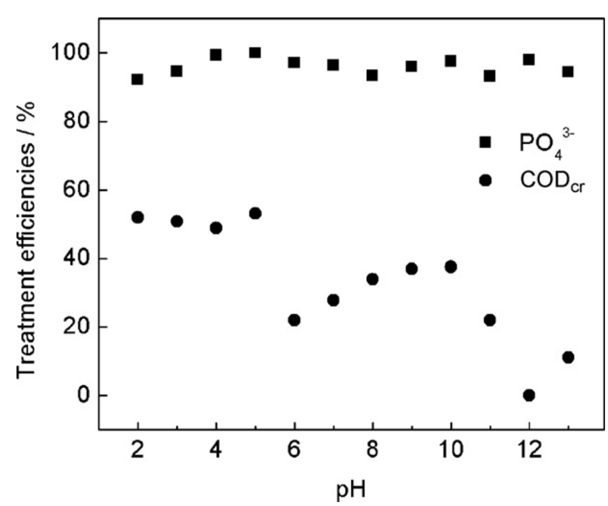

Fig. 4. pH effect on COD_{cr} and PO_4^{3-} removal efficiencies, respectively. Experimental conditions: temperature of 30 °C, modified honeycomb cinders dose of 10.0 g L^{-1}, reaction time of 20 min and settling time of 20 min.

Table 1
Elementary analysis of this experiment by EDS analysis.

Elementary analysis of this experiment by EDS analysis								
Raw honeycomb cinders			Modified honeycomb cinders			Precipitates after experiment		
Element	Wt%	at%	Element	Wt%	at%	Element	Wt%	at%
C	9.80	15.87	C	3.57	6.33	C	3.59	5.77
O	43.83	53.28	O	40.00	53.16	O	54.00	56.25
Na	0.44	0.37	Na	0.17	0.16	Na	0.69	0.58
Mg	0.59	0.47	Mg	0.49	0.43	Mg	0.48	0.38
Al	14.79	10.66	Al	14.30	11.27	Al	8.61	6.17
Si	23.80	16.48	Si	31.24	23.65	Si	29.99	20.65
S	0.33	0.20	S	0.11	0.07	S	0.09	0.05
K	1.85	0.92	K	2.12	1.15	K	1.18	0.59
Ca	0.80	0.39	Ca	1.40	0.74	Ca	0.34	0.16
Ti	0.77	0.31	Ti	0.86	0.38	Ti	0.20	0.08
Fe	3.00	1.04	Fe	3.58	1.36	Fe	0.72	0.25
			Cl	2.15	1.29	Cl	0.10	0.05
Matrix	Correction	ZAF	*Matrix*	Correction	ZAF	*Matrix*	Correction	ZAF

3.3. Temperature

Fig. 5 shows that the COD_{cr} removal efficiency could be improved from 40.0% to 72.4% with temperature increased from 30 °C to 60 °C, but remarkably decreased with temperature increased from 70 °C to 90 °C. The former indicated that chemical adsorption occurred for the removal of COD_{cr} because chemical adsorption is an endothermic process and temperature should favour COD_{cr} uptake, but the latter implied that physical adsorption also occurred for the removal of COD_{cr} for physical adsorption is an exothermic process and temperature should negatively influence phosphate uptake. Therefore, the removal mechanisms of COD_{cr} were likely attributed by both physical and chemical adsorptions. The maximum removal efficiency of COD_{cr} obtained at 60 °C was most likely due to the balance of physical and chemical adsorptions, the decrease of the removal efficiency from 60 °C to 90 °C might be implied that desorption phenomena appeared in physical adsorption. The PO_4^{3-} removal efficiency was only slightly increased from 93.4% to 99.2% with temperature changed from 30 °C to 90 °C, since it might be mainly attributed by chemical adsorption. Therefore, considering the simultaneous removals of COD_{cr}, and PO_4^{3-} as well as the cost of treatment, the operation temperature was selected as 60 °C.

3.4. Honeycomb cinders dose

Fig. 6 shows that, when the honeycomb cinders dose were at 30.0 g L^{-1}, the COD_{cr} and PO_4^{3-} removal efficiencies could be achieved to be 58.2% and 99.4%, respectively. When the honeycomb cinders dose were less than 30.0 g L^{-1}, both COD_{cr} and PO_4^{3-} removal efficiencies were decreased. When honeycomb cinders dose were more than 30.0 g L^{-1}, the COD_{cr} removal efficiency decreased by 2.4–4.8%, whereas the removal efficiency of PO_4^{3-} increased by 0.6% compared with that of the 30.0 g L^{-1} case. Therefore, it is evident that increasing dosage of honeycomb cinders could not substantially improve the COD_{cr} and PO_4^{3-} treatment efficiencies yet the treatment cost rises. Consequently, 30.0 g L^{-1} of honeycomb cinder was considered for the treatment process.

3.5. Reaction time

As shown in Fig. 7, when reaction time was increased from 20 min to 70 min, the COD_{cr} removal efficiency increased slowly but decreased significantly with reaction time increased from 70 min to 80 min. It was likely because that the removal mechanisms of COD_{cr} were attributed by both physical and chemical adsorptions. When the reaction time was increased from 70 min to 80 min, the removal efficiency of COD_{cr} was decreased. It might be deduced that

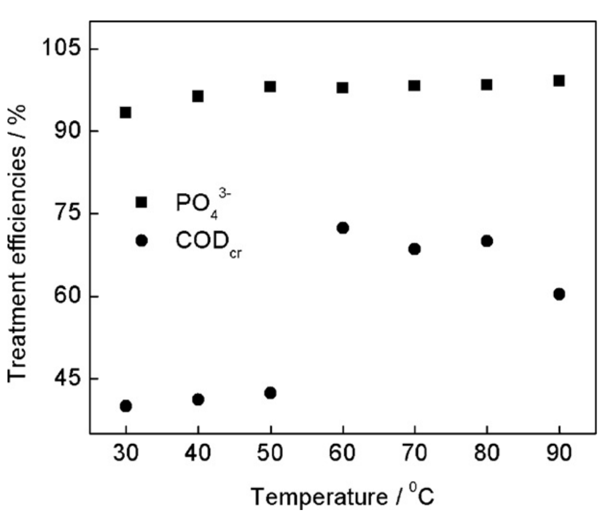

Fig. 5. Temperature effect on COD_{cr} and PO_4^{3-} removal efficiencies, respectively. Experimental conditions: pH of 5.0, modified honeycomb cinders dose of 10.0 g L^{-1}, reaction time of 20 min and settling time of 20 min.

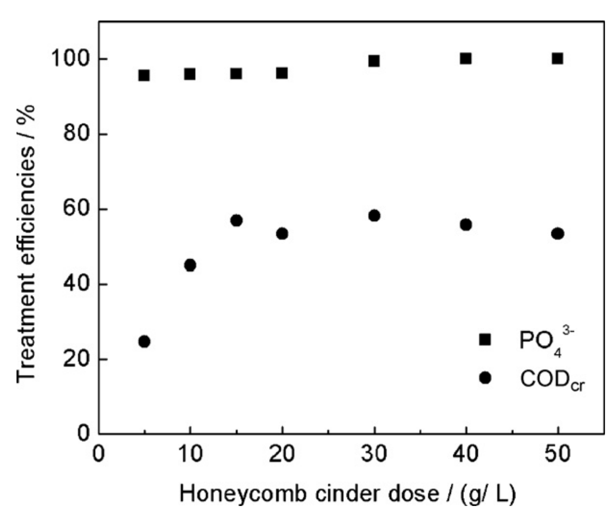

Fig. 6. Removal efficiencies of COD_{cr} and PO_4^{3-} under various dosages of modified honeycomb cinders. Experimental conditions: pH of 5.0, temperature of 60 °C, reaction time of 20 min and settling time of 20 min.

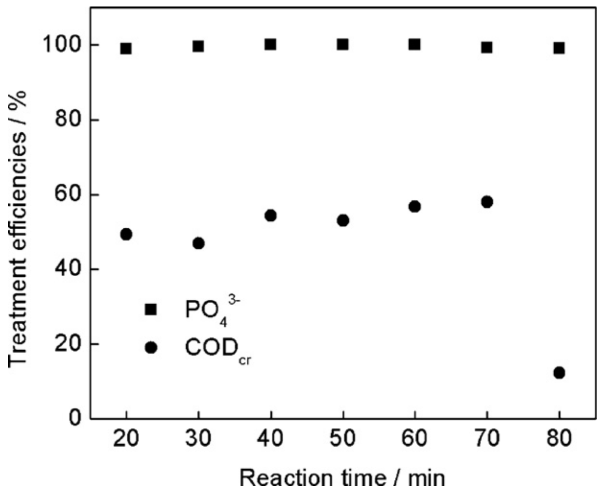

Fig. 7. COD_{cr} and PO_4^{3-} removal efficiencies under various reaction times. Experimental conditions: pH of 5.0, temperature of 60 °C, modified honeycomb cinders dose of 30.0 g L^{-1}, and settling time of 20 min.

desorption phenomena appeared in physical adsorption when the reaction time exceeds the complete reaction time. However, PO_4^{3-} removal efficiency was changed little with the experiment going on, which was kept at the range of 98.9–100% since the quickly finished in *ca.* 25 min. To consider the removal efficiencies for both COD_{cr} and phosphate, 25 min could be selected as the suitable reaction time.

3.6. Settling time

From Fig. 8 it was evident that the removal efficiencies of COD_{cr} and PO_4^{3-} could be improved when the settling time was of 30 min, whereas the removal efficiency of COD_{cr} was decreased when the settling time increased from 30 min to 70 min. It seemed to that the COD_{cr} removal efficiency was more sensitive to the change of settling time than that of PO_4^{3-}. The maximum removal efficiencies of COD_{cr} (66.7%) and PO_4^{3-} (99.9%) could be achieved for 30 min of settling time. In addition, with combination of the data presented in Fig. 2C_1–C_3, after settled down for 30 min, the pollutants adsorbed by the honeycomb cinders could be effectively removed. Therefore, the optimal settling time was decided to be at 30 min.

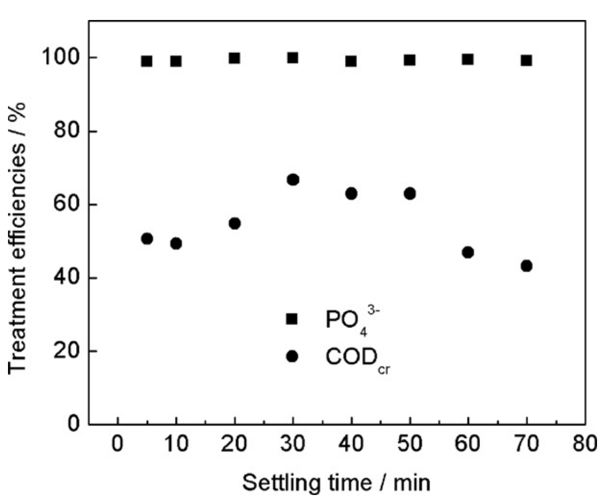

Fig. 8. Removal efficiencies of COD_{cr} and PO_4^{3-} under various settling time. Experimental conditions: pH of 5.0, temperature of 60 °C, modified honeycomb cinders dose of 30.0 g L^{-1}, reaction time of 25 min.

3.7. Discussion

When the PO_4^{3-} concentration was changed from 77 mg L^{-1} to 0 mg L^{-1}, the COD_{cr} was decreased from 6666 mg L^{-1} to 2222 mg L^{-1}. The treatment efficiencies of PO_4^{3-} and COD_{cr} were at 99.9% and 66.7%, respectively. Fig. 2 and Table 1 indicates that the modified honeycomb cinders adsorbed pollutants to be removed, though no obvious differences in Fig. 3. Thus, the treatment of landfill leachate by pretreated honeycomb cinders as an adsorbent could afford satisfactory results. The COD_{cr} in landfill leachate would be removed in the post-processing.

3.8. Economic estimation

The honeycomb cinders as an adsorbent in the present study were waste and free. This method was characterized by high removal efficiency, easy and steady operation, low cost, less occupied area, etc. The precipitates could be reused as paving material. In conclusion, the technology could offer an economically beneficial pretreatment way for landfill leachate treatment. It is also superior in lower sludge production, steadier running and more environmental friendliness, which is better than other physical and chemical treatments.

4. Conclusions

In this present work, the modified honeycomb cinders were found to be feasible for landfill leachate treatment with high removal efficiencies of simultaneous COD_{cr} and PO_4^{3-}. The optimal parameters were followed by: acidified honeycomb cinders of particle size less than 0.18 μm, pH of 5.0, temperature of 60 °C, honeycomb cinders dose of 30.0 g L^{-1}, reaction time of 25 min, and settling time of 30 min. The removal efficiencies of 66.7% for COD_{cr} and 99.9% for PO_4^{3-} were obtained by the proposed method. Furthermore, the structures and characteristics of raw/modified honeycomb cinders and resulting precipitates were probed by SEM, EDS and XRD. The high removal efficiencies of PO_4^{3-} and COD_{cr} revealed that the honeycomb cinders could initiate a new entry for the pretreatment of landfill leachate featured by operational simplicity, low cost, high efficiency, and eco-friend due to utilization of waste to treat waste.

Acknowledgments

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