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A study on using fireclay as a biomass carrier in an activated sludge system

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Abstract By adding a biomass carrier to an activated sludge system, the biomass concentration will increase, and subsequently the organic removal efficiency will be enhanced. In this study, the possibility of using excess sludge from ceramic and tile manufacturing plants as a biomass carrier was investigated. The aim of this study was to determine the effect of using fireclay as a biomass carrier on biomass concentration, organic removal and nitrification efficiency in an activated sludge system. Experiments were conducted by using a bench scale activated sludge system operating in batch and continuous modes. Artificial simulated wastewater was made by using recirculated water in a ceramic manufactutring plant. In the continuous mode, hydraulic detention time in the aeration reactor was 8 and 22 h. In the batch mode, aeration time was 8 and 16 h. Fireclay doses were 500, 1,400 and 2,250 mg l^{-1}, and were added to the reactors in each experiment separately. The reactor with added fireclay was called a Hybrid Biological Reactor (HBR). A reactor without added fireclay was used as a control. Efficiency parameters such as COD, MLVSS and nitrate were measured in the control and HBR reactors according to standard methods. The average concentration of biomass in the HBR reactor was greater than in the control reactor. The total biomass concentration in the HBR reactor (2.25 g l^{-1} fireclay) in the continuous mode was 3,000 mg l^{-1} and in the batch mode was 2,400 mg l^{-1}. The attached biomass concentration in the HBR reactor (2.25 g l^{-1} fireclay) in the continuous mode was 1,500 mg l^{-1} and in the batch mode was 980 mg l^{-1}. Efficiency for COD removal in the HBR and control reactor was 95 and 55%, respectively. In the HBR reactor, nitrification was enhanced, and the concentration of nitrate was increased by 80%. By increasing the fireclay dose, total and attached biomass was increased. By adding fireclay as a biomass carrier, the efficiency of an activated sludge system to treat wastewater from ceramic manufacturing plants was increased.

Keywords Fireclay · Ceramic · Wastewater · HBR

Introduction

Wastewater from refractory manufacturing plants is usually contaminated by non-organic compounds, heavy metals and finely dispersed suspensions of mineral materials. The concentration of suspended matter reaches 35 g l^{-1} [1]. Sedimentation tanks using coagulants are used to produce recyclable water [2, 3]. Usually wastewater from ceramic industries without secondary treatment is recycled or discharged into the sewers [4].

Activated sludge (AS) processes combined with a biofilm reactor such as the Trickling Filter (TF) or Rotating Biological Contactor (RBC) and activated sludge using a biomass carrier are called a Hybrid Biological Reactor (HBR). In the (AS-TF) and (AS-RBC), the volume of the system is greater than in conventional AS systems. The performance of the AS process for wastewater treatment can be improved by the addition of a biomass carrier in the aeration tank. Because of microbial growth on the biomass carrier surface, addition of these materials in the reactor will lead to increasing the biomass concentration. Application of a biomass carrier into the

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AS process will increase the treatment capacity without addition in the volume of the aeration tank. Moreover, the resultant sludge has good settling properties. The HBR system using mineral powders (clinoptilolite and bentonite) was compared with the conventional AS system, and the reported biomass concentration in the HBRs was greatly increased by biofilm formation on the powders [5].

Macro or micro carriers can be used as a biomass support medium. Macro carriers such as synthetic fiber or plastic media are fixed and occupy a large volume in the aeration reactor. Micro carriers (less than 1 mm in size) are suspended in the reactor without reducing the effective volume of tanks. These materials provide a large surface area for the immobilization of microbes and are easy to handle. If the biomass carrier has an adsorptive capacity for toxic compounds, the biological growth will be enhanced. The HBR system using polyurethane foam as a bio-carrier was developed, and the reported total biomass concentration in the hybrid reactors increased when the volumetric portion of the carrier was 15–30% [6]. Powdered activated carbon is one of the most effective bio-carriers, but it is an expensive material, and its application at large-scale wastewater treatment plants is restricted [7, 8]. Some researchers focused their study on finding alternative cheap materials to use in the AS system in order to improve efficiency. Alternative mineral materials such as talc, zeolite, clinoptilolite and bentonite have been studied [9–12].

Extracellular polymeric substances in the AS system and AS dosed with clinoptilolite were compared, and it was concluded that effluent quality could be enhanced to the highest rate of 95% [13].

Natural zeolite was used as a bio-carrier in an anaerobic fluidized bed reactor, and excellent physical characteristics of zeolite as a support medium were observed using scanning electronic microscopy [14].

The aim of this study was to investigate the possibility of using fireclay as a biomass carrier in the activated sludge system and to clarify the effect on the biomass concentration, COD removal and nitrification in the batch and continuous modes separately without and with the addition of fireclay.

Materials and methods

Two AS reactors were used. Each reactor consisted of a 6.5-l aeration unit and 3.5-l clarifier. One was used as a control without dosing mineral powder, and the other (HBR) was operated with the addition of fireclay as a biomass carrier. Both reactors were operated in two modes, batch and continuous. Experiments in batch mode were conducted using two aeration times, 8 and 16 h. In the continuous mode aeration times were 8 and 22 h. Different concentrations of fireclay (500, 1,400 and 2,250 mg l^{-1}) were maintained in the aeration unit of the HBR. AS reactors were seeded by sludge from a domestic wastewater treatment plant in Sari, Iran. Data analysis was performed after a 4-week start-up period. Reactors were operated at 20 ± 3°C, and dissolved oxygen concentration was maintained at 3–4 mg l^{-1}. Synthetic wastewater was employed as an influent in two reactors. Recycled water in a ceramic factory in Sari, Iran, was used to make simulated synthetic wastewater. In order to provide the nutrients necessary to biomass growth, the following compounds were added to recycled water: dry milk powder: 100 mg l^{-1}, sodium acetate: 50 mg l^{-1}, glycerol: 20 mg l^{-1}, peptone: 10 mg l^{-1}, urea: 40 mg l^{-1}, phosphate buffer: 2 mg l^{-1}, K_2HPO_4, $FeCl_3{\cdot}6H_2O$, $CaCl_2{\cdot}2H_2O$, $MgSO_4{\cdot}7H_2O$, each at 2 mg l^{-1}. Influent pH was controlled at 7–7.5 with bicarbonate buffer, and its alkalinity ranged from 500 to 600 mg l^{-1} as $CaCO_3$. By withdrawing excess sludge from the aeration basin and ignoring effluent suspended solids, a 10-day sludge retention time was maintained. The average concentrations of chemical oxygen demand (COD), total Kjeldahl nitrogen (TKN) and total phosphorus (TP) in the synthetic wastewater were maintained at 300, 50 and 5 mg l^{-1}, respectively. As a model of mineral material used in refractory manufacturing plants, fireclay was selected to simulate the condition. Fireclay used in this study was commercial grade and was washed several times with distilled water and then put in the furnace at 550°C for thermal decomposition of organic impurities. The treated fireclay was used as a biomass carrier. Different concentrations of fireclay (500, 1,400 and 2,250 mg l^{-1}) were maintained in the aeration unit of HBR. In order to determine the concentration of suspended biomass, the total suspended solids dried at 103°C were determined after the filtration of the total content of the control reactor at the end of the experiment at each stage according to the Standard Methods book (APHA, 1998) (2540D) [15]. For determination of the attached biomass, the total content of the HBR reactor was filtered after the end of each stage of the experiment, and the suspended solids dried at 103°C were ignited at 550°C in the furnace (APHA, 1998) (2540E). Then the amount of biofilm attached to the fireclay particles was determined by subtracting total biomass concentrations in the HBR and control reactor. This speculation is reasonable with the assumption that concentrations of suspended biomass in the control reactor are equal to those in the HBR reactor, because the two reactors are operated under comparable substrate and operating conditions. Some researchers used the same method to determine the attached biomass concentration [16]. Furthermore, the influence of the attached microorganisms on the growth condition of the suspended biomass was reported to be negligible [17].

Measured soluble COD in the recycled water of the ceramic factory was in the range of 250–300 mg l^{-1}. In the

Fig. 1 Photo of the reactor used in this study

batch mode, the recycled water was diluted, and then nutrients were added to it. For batch mode, the influent COD after the addition of nutrients was in the range of 320–400 mg l^{-1}. In the continuous mode, recycled water was not diluted, and after adding nutrients, the influent COD was in the range of 500–540 mg l^{-1}. COD was measured by a closed reflux titrimetric method (APHA, 1998) (5220 D).

In order to determine the effect of adding a biomass carrier to the nitrification, experiments were conducted by operating the HBR reactor continuously for more than 40 days. The concentration of fireclay in the reactor during this stage was 2,250 mg l^{-1}. NO_3-N was measured by the spectrophotometeric method (ASTM, Method 352.1). All data are the average of three separate experiments in each mode. The experimental setup used in this study is shown in Fig. 1.

Results and discussion

Biomass concentration

Batch operations were conducted at two aeration times: 8 and 16 h, respectively. The concentrations of fireclay in the HBR reactors were 500, 1,400 and 2,250 mg l^{-1}. In the control reactor, conditions such as DO, wastewater composition and operation parameters were the same as in the HBR.

The concentration of biomass in the control reactor during the operation was averaged at 1,410 mg MLVSS/l (dry weight). Biomass concentration in the control reactor was low; the reason may be related to the presence of toxic materials in the wastewater (or recycled water) of the ceramic plant. Some studies show that wastewater from ceramic industries contains toxic matter such as boron [18]. In the HBR reactor, the biomass concentration compared with the control was increased. The average biomass concentration in the HBR reactor using 500 mg l^{-1} fireclay as a biomass carrier was 1,600 mg MLVSS/l. When the concentration of fireclay in the reactor was 2,250 mg l^{-1}, the biomass concentration was obtained at 2,060 mg l^{-1}. In the HBR, with increasing fireclay dose, the biomass concentration increased very slightly. The results are shown in Table 1.

In the batch mode at 16 h aeration time, the microbial concentration in the HBR with 2,250 mg l^{-1} of fireclay was 700 mg l^{-1} higher than those with 500 mg l^{-1} mineral concentration. This indicates that biofilm is formed on the fireclay particle surfaces. The ratio of mineral concentration to the attached growth biomass concentration was in the range of 2.63 (500:190) to 3.46 (2,250:650) with 8 h aeration time. This did not indicate that the attached growth biomass concentration was linearly proportional to the amount of fireclay dosed. In cases in which a high concentration of biomass was attached to mineral particles in the HBRs, the greater part of the substrate can be consumed by the biofilm [17]. Namely, organic matter can be utilized by the biofilm formed on the surface of the fireclay particles. This suggests that the attached biofilm in the HBRs would greatly contribute to organic matter removal. Furthermore, fireclay particles may adsorb toxic compounds in the ceramic wastewater that harm the biomass.

Table 2 shows the biomass concentration in the HBR and control reactor in continuous operation mode. Aeration times were 8 and 22 h, respectively. As can be seen from Table 2, biomass concentration in the continuous mode was

Table 1 Biomass concentration in the HBR and control reactors

Aeration time (h)	Reactor type	Fireclay conc. (mg l^{-1})	Total biomass (mg MLVSS l^{-1})	Attached biomass (mg MLVSS l^{-1})
8	Control	0	1,410	0
	HBR	500	1,600	190
		1,400	1,920	510
		2,250	2,060	650
16	Control	0	1,420	0
	HBR	500	1,700	280
		1,400	2,100	680
		2,250	2,400	980

Table 2 Biomass concentration in the HBR and control reactors in the continuous mode

Aeration time (h)	Reactor type	Fire clay conc. (mg l^{-1})	Total biomass (mg MLVSS l^{-1})	Attached biomass (mg MLVSS l^{-1})
8	Control	0	1,680	0
	HBR	500	2,130	450
		1,400	2,900	1,220
		2,250	3,200	1,520
22	Control	0	1,500	0
	HBR	500	2,050	550
		1,400	2,400	900
		2,250	3,000	1,500

Table 3 Experimental results on COD removal efficiency by HBR reactors (runs 1 and 2) and comparison with control reactor

Parameters	Batch mode			Continuous mode		
	Control	Run 1	Run 2	Control	Run 1	Run 2
Influent COD (mg l^{-1})	320–400	320–400	320–400	500–540	490–530	490–530
Average COD_{in} (mg l^{-1})	357	357	357	510	505	505
HRT (h)	8	8	16	8	8	22
Effluent COD (mg l^{-1})	140–180	0–50	0–30	280–310	90–100	20–30
Average COD_{eff} (mg l^{-1})	160	40	15	290	95	25
% COD removal	55	88	95	43	81	95
Fireclay dose (mg l^{-1})	0	2,250	2,250	0	2,250	2,250
Total biomass (mg l^{-1})	1,420	2,060	2,400	1,680	3,200	3,000
Suspended biomass (mg l^{-1})	1,420	1,410	1,420	1,680	1,680	1,500
Attached biomass (mg l^{-1})	0	650	980	0	1,520	1,500

greater ($P < 0.05$) than in the batch mode. The hybrid reactor had higher biomass concentrations ($P < 0.05$) than the control because of the addition of a biomass carrier and the formation of an attached growth biomass.

The average total biomass concentrations in hybrid reactors were 1.26–1.9 times higher than in the control reactors without adding biomass carriers. The average attached growth biomass concentrations in a hybrid reactor were 450–1,500 mg l^{-1}, which consisted of 20–50% of the total biomass concentration. This indicates that the attached growth biomass played a considerable role in COD removal in the hybrid reactor or some compounds adsorbed on fireclay particles. Tables 1 and 2 also indicate that the attached growth biomass concentrations were influenced by the amount of biomass carrier added in the reactor. By increasing the amount of biomass carrier in the reactor, the amount of attached biomass was increased.

COD removal

The COD removal efficiency observed in the HBR and control reactor under different conditions is illustrated in Table 3. Experiments were performed at two COD ranges. The experimental results are summarized in Table 3. In the batch mode during run 1, the COD concentrations in effluents ranged from 0 to 50 mg l^{-1} in all reactors where the average removal efficiencies were similarly attained at approximately 88%. For run 2 efficiencies of COD reduction were also favorably obtained at 95% in the reactors. While the HBR reactor operated under 2,250 mg l^{-1} of fireclay concentration, it presented an average COD removal efficiency of 33% higher than that in the control reactor, as expected.

This was because high concentrations of biomass were formed in the HBRs compared to the control ($P < 0.05$). In run 2, the aeration time was extended to 16 h; with the same influent COD in run 1, the COD of effluent in run 2 ranged from 0 to 30 mg l^{-1}, and the removal efficiency reached 95%. In the continuous mode the influent COD was higher than in the batch mode. The average influent COD in 16 separate experiments in continuous mode was 510 mg l^{-1}. In this stage COD removal was restricted in all reactors. In general, the percentage of COD removed decreased with increased organic loading rates over the ranges applied in this investigation. More than 80% feed COD could be removed, which indicates that this hybrid system was highly effective. At higher organic loading rates, the COD removal efficiency decreased by only 7%.

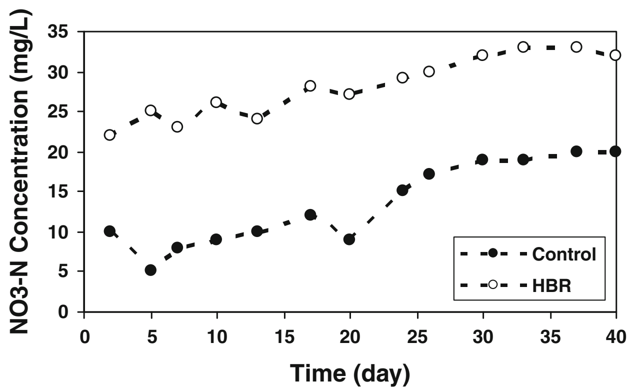

Fig. 2 Comparison of NO_3-N concentration with time in the HBR and control reactors

Nitrification

Figure 2 shows variations in NO_3-N concentrations with time in the continuous HBR and control reactors with 8 h aeration time. As can be seen from this figure, the concentration of nitrate was increased in both the control and HBR reactors. However, nitrification in the HBR reactor was higher than in the control reactor. Nitrification was favorably obtained in the HBR and control reactor after 40 days of operation duration.

Factors affecting competition between heterotrophs and nitrifiers in commonly referred to biofilms are: (1) internal mass transfer resistance for $NH4^+$-N and (2) oxygen diffusion limitation from accumulation of heterotrophs in the outer biofilm. It is suggested that the influence of oxygen diffusion limitation may correspondingly occur in both HBRs with similar biomass and DO concentration. If a mineral such as clinoptilolite has a high ammonium exchange property, it can provide a driving force to overcome internal mass transfer resistance for NH_4^+-N. Therefore, it can be concluded that the ammonium exchange capacity of fireclay enables nitrifiers to colonize favorably in the biofilm attached to this mineral, and this enhances nitrification [11, 19]. Furthermore, fireclay particles may adsorb some compounds, resulting in adverse effects on nitrifires in solution, and nitrification may be improved as a consequence of decreased inhibition [5].

Conclusion

Mineral sludge resulting from the water recovery system of ceramic, brick and tile manufacturing industries can be used as a biomass carrier for treatment of wastewater in these plants by an activated sludge system. By using mineral material particles as the biomass carrier, the total biomass in the aeration tank, including attached and suspended biomass, COD removal efficiency and nitrification capability were increased.

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