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ORIGINAL PAPER

Influence of nickel (II) and chromium (VI) on the laboratory scale rotating biological contactor

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Abstract High concentration of heavy metals is toxic for most microorganisms and cause strict damage in wastewater treatment operations and often a physico-chemical pretreatment prior to biological treatment is considered necessary. However, in this study it has been shown that biological systems can adapt to Ni (II) and Cr (VI) when their concentration is below 10 and 20 mg/L, respectively. The aim of this study was to evaluate the effect of Ni (II) and Cr (VI) on the lab-scale rotating biological contactor process. It was found that, addition of Ni (II) up to 10 mg/L did not reduce the chemical oxygen demand removal efficiency and on the contrary concentrations below 10 mg/L improved the performance. The influent Ni (II) concentration of 1 mg/L was the concentration where the treatment efficiency produced a maximum COD removal of 86.5%. Moreover, Ni (II) concentration above 10 mg/L was relatively toxic to the system and produced lower treatment efficiencies than the baseline study without Ni (II). Turbidity and suspended solids removals were not stimulated to a great extent with nickel. Addition of Ni (II) did not seem to affect the pH of the system during treatment. The dissolved oxygen concentration did not drop below 4 mg/L at all concentrations of Ni (II) indicating aerobic conditions prevailed in the system. Experiments conducted with Cr (VI) revealed that addition of Cr (VI) up to 20 mg/L did not reduce the COD removal efficiency and on the contrary concentrations below 20 mg/L improved the performance. The influent Cr (VI) concentration of 1 mg/L was the concentration where the treatment efficiency produced a maximum COD removal of 88%. Turbidity and SS removals were more efficient at 5 mg/L Cr (VI) concentration, rather than 1 mg/L, which lead to the conclusion that 5 mg/L Cr (VI) concentration is the optimum concentration, in terms of COD, turbidity and SS removals. Similar with Ni (II) experiments, addition of Cr (VI) did not significantly affect the pH value of the effluent. The DO concentration remained above 5 mg/L.

Keywords Nickel (II) · Chromium (VI) · Rotating biological contactors · Biological treatment · Chemical oxygen demand

Introduction

The rotating biological contactor process (RBC) is a secondary biological wastewater treatment system for the treatment of domestic and industrial wastewaters of organic origin. In this process a series of closely spaced disks, 2–3 m in diameter are mounted on a common horizontal shaft, and placed in a semi-cylindrical tank. The contactor is slowly rotated while approximately 40% of the surface area is submerged in the wastewater. Immediately after start-up, organisms naturally present in the wastewater begin to adhere to the rotating disks and multiply within 1 week, until the entire surface area is covered with a layer of biomass approximately 1–4 mm in thickness. The attached biomass permits high degrees of treatment to be achieved with relatively short wastewater retention times. During rotation, the contactor carries a film of wastewater into the

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air, which trickles down to the surfaces and absorbs oxygen from the air. The biological growth on the disk surfaces assimilate the organic materials present in the wastewater and produce carbon dioxide and new cellular material as a result. Aeration is provided by the rotating action which exposes the disks alternating to the air and to the wastewater. Excess biomass is sheared off into the tank, where the rotating actions of the disks maintain the solids in suspension. Eventually, the flow of the wastewater carries these solids out of the system and into a clarifier, where they are separated. The factors controlling the performance of operation in a rotating biological contactor process are disk rotational speed, staging, wastewater temperature, flowrate, liquid retention time and strength of influent wastewater.

Heavy metals are regarded as a major group of toxic pollutants. The most important fact distinguishing the heavy metals from other toxic pollutants is that they are not biodegradable and their potential toxicity in the environment is controlled to a great extent by biological and geochemical factors. The presence of heavy metals in wastewaters, mostly originating from industries is of concern since their discharges into the receiving waters may be detrimental to the environment, and also a reduced efficiency in biological wastewater treatment may occur.

There is a plenty of data regarding the effect of heavy metals on the activated sludge process. It was stated [1] that relatively low concentrations of heavy metals may serve to stimulate biological systems and increase the rate of biological reaction. However, further increase in metal concentration reduces the reaction rate and results in failure of the system. It was reported [2, 3] that the inhibiting concentration of cadmium, chromium and nickel on biological process occurs at above 10 mg/L. Similarly, Ni (II) concentration higher than 10 mg/L was found toxic to the activated sludge. Moreover, 10 mg/L Cr (VI) had no adverse effect on the activated sludge unit and chemical oxygen demand (COD) removal was not lower than 85% at 25 mg/L Cr (VI) [4]. It was reported [5] that the addition of 5 mg/L Ni (II) caused a slight reduction in total organic carbon (TOC) removal efficiency, whereas 10 mg/L Ni (II) significantly affected the sequencing batch reactor performance in terms of suspended solids and TOC removal efficiency. It was stated [6] that all the heavy metals investigated were tolerable in raw sewage at concentrations below 1 mg/L depending on the unit process and the metal involved, concentrations up to 20 mg/L might have no inhibitory effect. Threshold concentrations were found as 1, 10, 20, 20, 5, 1 and 10 mg/L for chromium, cadmium, copper, lead, mercury, nickel and zinc, respectively.

There is little information available in the literature to describe the effect of chromium and nickel on a RBC treatment system. It was stated [7] that RBC process was suitable for metal concentrations of up to 30 mg/L lead and 10 mg/L nickel and copper with minor reductions in treatment efficiency. The RBC system was reported [8] to operate successfully over an extended period of time with removal efficiencies of 34, 85 and 57% for Cd^{2+}, Cu^{2+} and Zn^{2+}, respectively. The 3-stage RBC system to treat wastewater contaminated with Cd, Cu and Zn was reported to successfully remove the metals in the order Cu > Zn > Cd with removal capacities of 73, 42 and 33%, respectively [9]. In another study, different levels of cadmium (5 and 20 mg/L) were dosed to a 3-stage RBC unit. Experimental results indicated that the treatment efficiency varied from 85 to 95% [10].

It is the aim of the present study to report on the effect due to Ni (II) and Cr (VI) on the laboratory-scale RBC treatment method. To that end, different Ni (II) and Cr (VI) concentrations were tested in a RBC, using synthetic wastewater.

Materials and methods

Wastewater

A sterilized synthetic wastewater made up by mixing three different solutions was used throughout the experiments. The solutions were prepared separately and added to the bulk solution containing water and meat extract to give the overall composition in Table 1. A synthetic wastewater was prepared and stored in a 20 L glass bottle. From this bottle the flow was directed to an equalizing tank with about 5 L capacity at which the water level was kept constant by a float to provide constant flow to the RBC unit. The inflow rate to the RBC was controlled by a valve.

Laboratory scale RBC system

A laboratory scale RBC system was housed in a steel semicylinder, 48-cm long and 23-cm in diameter and composed of five compartments namely primary sedimentation, three stages of RBC and final sedimentation tank (Fig. 1). The wastewater passed from one compartment to the next over the dividing plates. The total liquid volume of the three RBC stages was 1.2 L. A horizontal steel shaft supported nine disks (3 disks per stage), each 22 cm in diameter, giving a total submerged disk surface area of 0.2268 m^2. A total of 40% of the disks were submerged in the liquid and the total wetted surface area of the disks was 0.6566 m^2. The disks were made of corrugated aluminum plates, manufactured in Turkey. Liquid volume/surface area was 5.29 L/m^2. The operating conditions were such that the flowrate was 5 L/d, hydraulic loading rate was 22 L/d/m^2surface, organic loading rate was 14.32 g. COD/m^2/d and the liquid retention times were approximately 2 h for primary sedi-

Table 1 Chemical composition of stock solutions

Component	Constituents	Concentration (mg/L)	Amount of components in 1 L of synthetic wastewater (mL)
Solution 1	$MnSO_4 \cdot H_2O$	68.83	1.9
	MoO_3	30.00	
	NaOH	8.35	
	$ZnSO_4 \cdot 7H_2O$	87.89	
	$CoCl_2 \cdot 6H_2O$	80.78	
	$CuSO_4 \cdot 5H_2O$	81.70	
Solution 2	KH_2PO_4	25	1.0
	Na_2SO_4	25	
Solution 3	$MgCl_2 \cdot 6H_2O$	10	0.4
	$FeCl_2 \cdot 4H_2O$	12.21	
	$CaCl_2 \cdot 2H_2O$	10	
Meat extract	Protease–peptone oxoid	125	–
Tap water	–	–	996.7

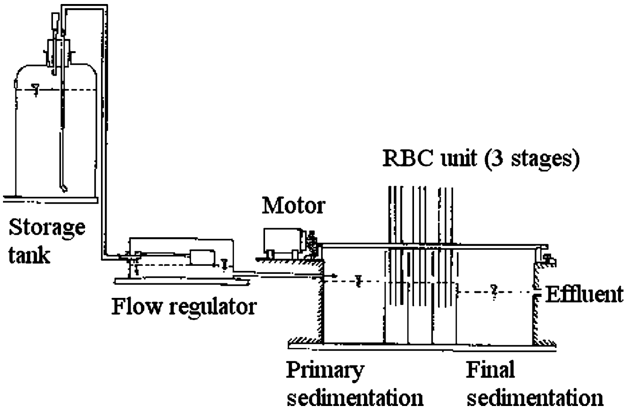

Fig. 1 Laboratory scale RBC system

mentation, 5 h for the RBC and 4 h for the secondary sedimentation units. The disks rotational speed was 6 rpm.

RBC experiments

Experimental studies were carried out to determine the effects of Ni (II) and Cr (VI) on the treatment efficiency of the RBC unit by adding these metals into sterilized synthetic wastewater to give varying concentrations. Ni (II) was supplied in the form of $NiCl_2 \cdot 6H_2O$ (Merck, product code: 1.06717) and the tested Ni (II) concentrations were 1, 5, 10, 15 and 20 mg/L. At the end of nickel studies, reactor was cleaned and chromium studies were performed with renewed culture. Cr (VI) was supplied in the form of $K_2Cr_2O_7$ (Merck, product code: 8.22266) and the tested Cr (VI) concentrations were 1, 5, 10, 15, 25, 50 and 75 mg/L.

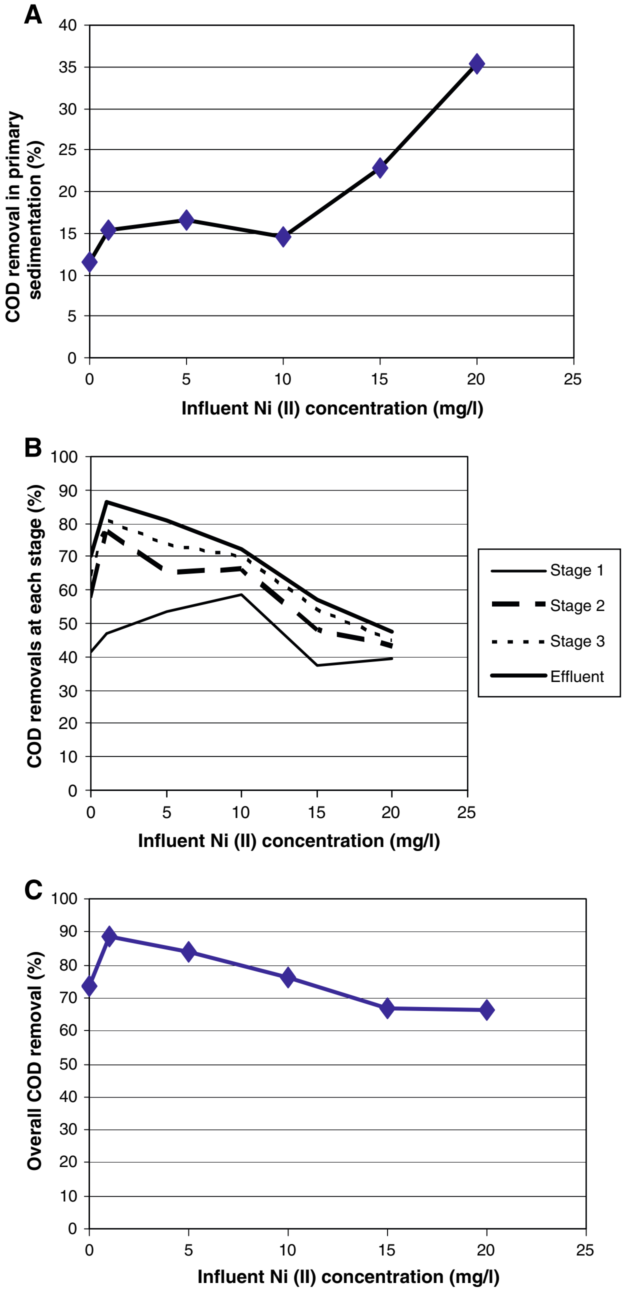

Fig. 2 Results of experiments conducted with Ni (II) [percent COD removal in primary sedimentation (**a**), percent COD removals at each stage in RBC unit and in the effluent of RBC unit (**b**) and overall COD removals including primary sedimentation, 3-stage RBC unit and the secondary sedimentation unit (**c**)]

The performance of the process was observed by monitoring COD removal. Duplicated samples were taken from the effluents of the primary sedimentation, at each stage of the RBC and from the secondary sedimentation tank. At each concentration of Ni (II) and Cr (VI) tested, measurements were carried out for pH, turbidity, dissolved oxygen (DO) and suspended solids (SS) after the percent COD removal values reached to a steady state.

Analysis

The micro-COD method has been applied for COD analysis. Two microliter of sample and a solution containing 2.5 mL H_2SO_4, 0.0245 g $K_2Cr_2O_7$, 0.03 g $AgSO_4$ and 0.03 g $HgSO_4$ were added into vials. After placing the caps, the vials containing samples and blanks were kept in a heating block at 150 °C for 2 h. COD values were measured by a UV–visible spectrophotometer (Beckman Coulter) as absorbance at a wavelength of 620 nm [11]. The absorbance values were converted to COD values by consulting to a calibration curve prepared beforehand by various concentrations of COD equivalents of phtalic acid.

Dissolved oxygen, pH and turbidity were measured by using a DO meter (YSI DO meter, Argent (E-DO-YS-58-MTR), digital pH meter (Beckman Coulter) and Hach-Turbidimeter, respectively. SS measurements were carried out according to the standard methods [12]. The influent and effluent samples were filtered through 0.45 µm pore size Whatman membrane filters using a Millipore vacuum pump. The filter paper was dried to a constant weight at 200 °C for 2 h.

Results

Experiments conducted with Ni (II)

The performance of the process was observed by COD removal. The sterilized synthetic wastewater was prepared to maintain a constant influent concentration of about 650 mg/L. Samples were taken from the effluents of the primary sedimentation, at each stage of the RBC and from the secondary sedimentation tank. When percent COD removal between the effluents of primary and secondary sedimentation units approached to a steady constant value, the analyses were carried out for the other parameters namely pH, DO, turbidity and SS. These were analyzed at the influent and effluent of the RBC units. Experimental studies were carried out to determine the effects of Ni (II) on the treatment efficiency of the RBC unit by adding nickel into the synthetic wastewater to give varying concentrations.

Baseline study was performed to eliminate the possibility of the influent COD concentration affecting the results. To study the effects of Ni (II) on the RBC, the model RBC unit was initially operated as a control, only receiving synthetic wastewater devoid of nickel. The COD removal was 70.1% in the RBC unit fed by synthetic wastewater devoid of nickel and when only the effluents from primary and secondary sedimentation units were considered.

The experimental studies with Ni (II) have been carried out for about 3 months. The COD removals in the primary sedimentation were observed as 11.5, 15.4, 16.6, 14.6, 22.8 and 35.4% at 0, 1, 5, 10, 15 and 20 mg/L influent Ni (II) concentrations, respectively (Fig. 2a). Figure 2b shows the treatment efficiency of each stage of the RBC unit with tested concentrations of Ni (II) and revealed that nickel stimulated the treatment efficiency. Addition of Ni (II) up to 10 mg/L did not reduce the removal efficiency and on the contrary concentrations below 10 mg/L improved the

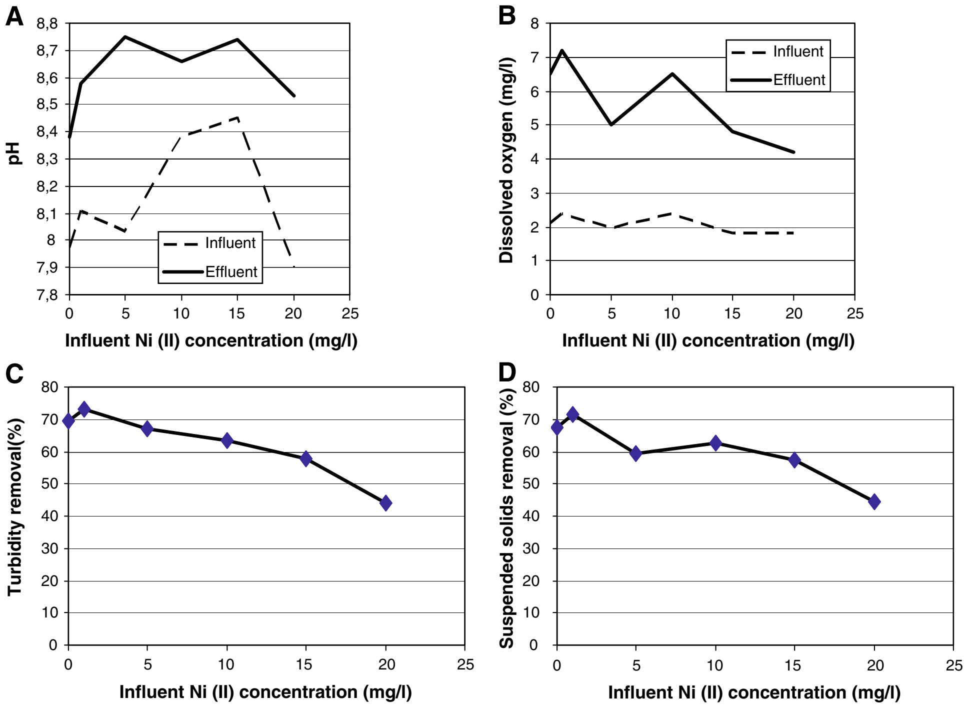

Fig. 3 Results of experiments conducted with Ni (II) [change in pH (**a**), change in DO (**b**), percent turbidity removal (**c**) and percent SS removal (**d**)]

performance. The influent Ni (II) concentration of 1 mg/L was the concentration where the treatment efficiency produced a maximum COD removal of 86.5% in the effluent of the RBC unit. Nickel (II) concentration above 10 mg/L (15 and 20 mg/L) was found to be relatively toxic to the system and produced lower treatment efficiencies than the baseline study. The most efficient COD removal was found to be in the first stage of the RBC unit. The COD removal efficiency in the first stage of the RBC unit increased gradually up to 10 mg/L Ni (II) concentration. The overall COD removals (Fig. 2c) including primary sedimentation and RBC treatment were 73.5, 88.6, 83.8, 76.1, 66.9 and 66.1% at 0, 1, 5, 10, 15 and 20 mg/L influent Ni (II) concentrations, respectively. A total of 1 mg/L Ni (II) concentration provided 88.6% overall COD removal and 10 mg/L Ni (II) concentration was again the threshold.

The effects of varying influent Ni (II) concentrations on pH, turbidity, DO and SS were also examined. RBC treatment increased the pH slightly and high pH values at the influent were related to the slightly alkaline character of the tap water and the components of the meat extract used (Fig. 3a). Dissolved oxygen concentrations increased at the effluent due to the aeration provided during the treatment and it was higher than 4 mg/L at all the experiments indicating aerobic conditions at all times (Fig. 3b). The turbidity removal of 69.3% without nickel addition was exceeded only at 1 mg/L Ni (II) concentration and reached to 73.3% removal (Fig. 3c). The percent SS removal (Fig. 3d) indicated that the removal of 67.6% in the influent without Ni (II) was increased to 71.4% when Ni (II) was 1 mg/L in the influent but did not produce better results at the higher influent Ni (II) concentrations. Similar to turbidity readings, effluent SS concentration also increased with the increasing influent Ni (II) concentrations.The biofilm thickness remained unchanged at 1 mg/L influent Ni (II) and without nickel conditions. A gradual decrease in the thickness was visually observed at 5 mg/L and higher Ni (II) concentrations. At 20 mg/L Ni (II) concentration, green flocs were observed on the biofilm. A gradual decrease in the thickness from the first to the last stage was observed throughout the study.

Experiments conducted with Cr (VI)

At the end of nickel studies, the reactor was cleaned and chromium studies were performed with renewed culture. In order to study the effects of Cr (VI) on the RBC, the model RBC unit was initially operated as a control, only receiving synthetic wastewater devoid of chromium. The COD removal was 74.7% in the RBC unit fed by synthetic wastewater devoid of chromium and when only the effluents from primary and secondary sedimentation units were considered.

The experimental studies with Cr (VI) have also been carried out for about 3 months. The percent COD removals in the primary sedimentation were observed as 33.1, 35.1, 30.0, 32.3, 26.2, 23.1 and 35.4% at 0, 1, 5, 10, 25, 50 and 75 mg/L influent Cr (VI) concentrations, respectively (Fig. 4a). Figure 4b shows treatment efficiency of the each stage of the

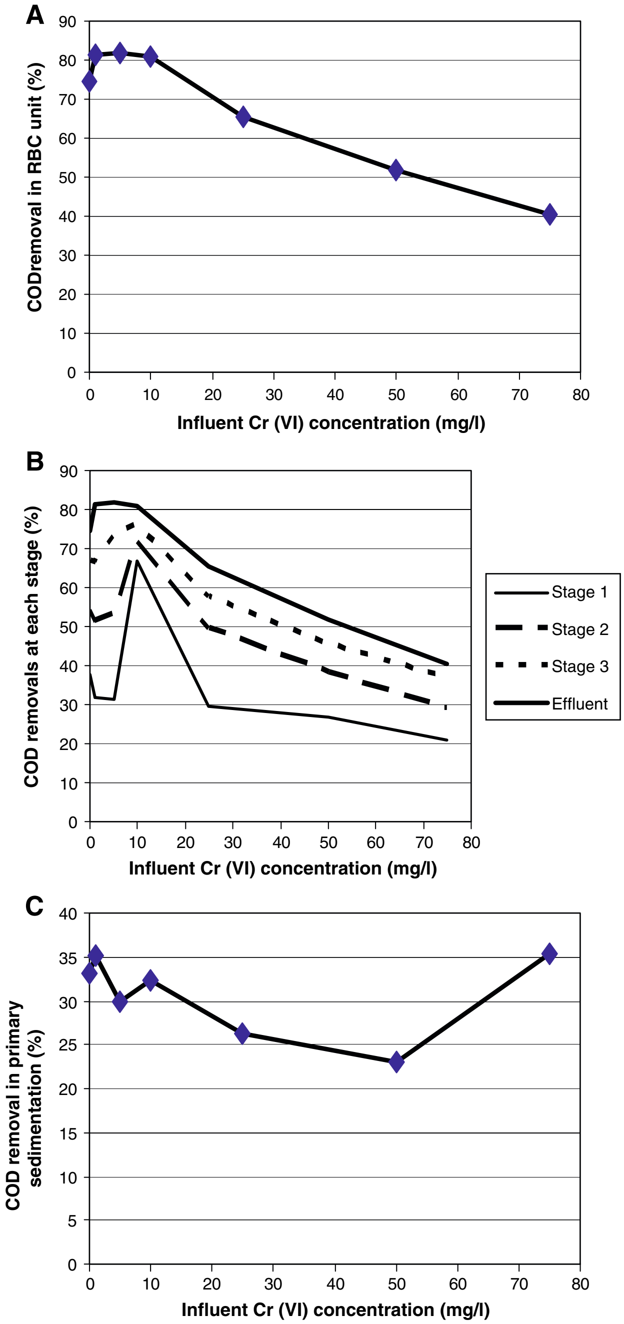

Fig. 4 Results of experiments conducted with Cr (VI) [percent COD removal in primary sedimentation (**a**), percent COD removals at each stage in RBC unit and in the effluent of RBC unit (**b**) and overall COD removals including primary sedimentation, 3-stage RBC unit and the secondary sedimentation unit (**c**)]

RBC unit with tested concentrations of Cr (VI). As can be seen from the figure, chromium stimulated the treatment efficiency. Addition of Cr (VI) up to 20 mg/L did not reduce the removal efficiency and on the contrary concentrations below 20 mg/L improved the performance. The influent Cr (VI) concentration of 1 and 5 mg/L concentrations resulted in very close COD removal efficiencies as 81.5% and 81.8% in the effluent of the RBC unit, respectively. Cr (VI) concentration above 20 mg/L (25, 50 and 75 mg/L) was found to be relatively toxic to the system and produced lower treatment efficiencies than the base line study without Cr (VI). Similar to the experiments conducted with Ni, the most efficient COD removal was found to be in the first stage of the RBC unit. The COD removal efficiency in the first stage of the RBC unit increased gradually up to 20 mg/L Cr (VI) concentrations. The overall COD removals including primary sedimentation and RBC treatment were found as 83.1, 88.0, 87.2, 86.9, 74.6, 63.1 and 61.5% for 0, 1, 5, 10, 25, 50 and 75 mg/L influent Cr (VI) concentrations, respectively. Figure 3c revealed the result that 1 mg/L Cr (VI) concentration provided 88.0% overall COD removal and 87.2% at 5 mg/L Cr (VI) concentration.

The effects of varying influent Cr (VI) concentrations on pH, turbidity, DO and SS were also examined. It was found that RBC treatment increased the pH slightly and high pH values at the influent were related to the slightly alkaline character of the tap water and the components of the meat extract used (Fig. 5a). DO concentrations increased at the effluent due to the aeration provided during the treatment. DO was higher than 5 mg/L at all the experiments indicating aerobic conditions at all times (Fig. 5b). The turbidity removal (Fig. 5c) of 62.5% without chromium addition was increased to 64, 66.7 and 64% at 1, 5 and 10 mg/L Cr (VI) concentrations, respectively. The percent SS removal (Fig. 5d) indicated that 5 mg/L influent Cr (VI) concentration provided better removal efficiency compared with the 1 mg/L Cr (VI) concentration. At 10 mg/L the removal efficiency approached to baseline study without Cr (VI) addition. The higher Cr (VI) concentrations as 25, 50 and 75 mg/L resulted in poorer effluent qualities.

The biofilm thickness remained unchanged at 1 mg/L influent Cr (VI) concentration. There was gradual decrease in thickness from the first towards the third stage of the RBC unit. At 5 mg/L Cr (VI) feed concentration, there was a noticeable increase in the biofilm thickness at the first stage which also remained the same at 10 mg/L Cr (VI) concentrations. At increased Cr (VI) concentrations the biofilm thickness decreased gradually.

Concluding remarks

The selected heavy metals, nickel and chromium were chosen deliberately as they are most common in many industrial wastewaters. Advantages of RBC process have made it a good alternative to the activated sludge especially in the case of industrial wastewater treatment. It was reported [13] that Cr (VI) and Cr (III) are ecologically important because

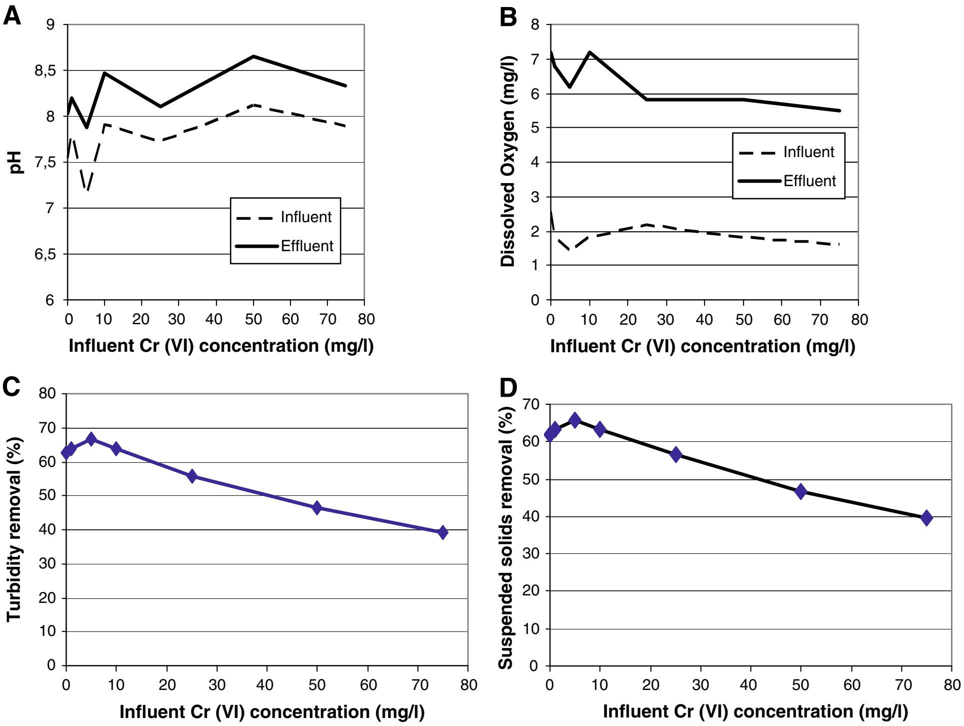

Fig. 5 Results of experiments conducted with Cr (VI) [change in pH (**a**), change in DO (**b**), percent turbidity removal (**c**) and percent SS removal (**d**)]

they are more stable oxidation states. Being mutagenic and carcinogenic, Cr (VI) is approximately 100-fold more toxic than Cr (III).

The effects of Ni (II) and Cr (VI) during the wastewater treatment process were separately investigated in the laboratory scale RBC process. To that end, different Ni (II) and Cr (VI) were tested in the RBC process using sterilized synthetic wastewater. The process was screened by checking removal percentages of COD.

Previous study stated [1] that relatively low concentrations of heavy metals may serve to stimulate biological systems and increase the rate of biological reaction. However, further increase in metal concentration reduces the reaction rate and results in failure of the system. This is confirmed by the laboratory scale RBC unit that seemed to operate satisfactorily throughout the study. In terms of COD removal, Ni (II) at a concentration of 1 mg/L appeared to be the optimum concentration, while 10 mg/L was the threshold value of toxicity. Similar to other studies [2–5, 7], the Ni (II) concentrations below 10 mg/L were found to be stimulating the COD removal efficiency, but were toxic to the system above this concentration.

The chromium concentrations of 1 and 5 mg/L provided similar COD removal efficiencies, the 5 mg/L Cr (VI) concentration being slightly higher. The recorded threshold concentration of toxicity was 20 mg/L, below which improvement of the COD removal efficiency was observed. Similar to previous studies [2, 3], at concentrations above this level, chromium was found to be toxic to the system. The 25 mg/L Cr (VI) concentration seemed to be tolerated by the activated sludge process [4], while the limit was 20 mg/L for the RBC unit.

Optimum surface loading rates giving the highest COD removals were not sought in this study and that was not within the scope of the study. However, it was apparent from the trend of the curves that a slight increase in COD and SS removal could be attained; if a fourth RBC stage in series existed. Alternatively, the hydraulic loading rate could be lowered for higher efficiency.

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