Behavior of redox potentials in artificial wetlands models: A tool for controlling its efficiency

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Experiments were carried out in a lab scale reactor artificial wetlands system in order to evaluate the role played by diffusion and photosynthesis phenomena using as a tool oxidation-reduction potentials (E_h). Four plastic 20-Liter lab scale reactors were made and filled with volcanic slag. Three commercial oxidation-reduction potential electrodes were placed at 2, 10, and 30 cm from top of each reactor and recording the E_h values through a computer. Illumination-darkness periods (16-8 h) were daily maintained with lamps imitating sunlight. Depuration efficiency was measured by using influent and effluent $COD_{soluble}$ (soluble chemical oxygen demand) of each reactor. Synthetic water was used and daily prepared by dissolving sucrose, $(NH_4)_2SO_4$ and Na_3PO_4. Results obtained indicate that photosynthetic phenomena have an important effect in the $COD_{soluble}$ removal since the planted reactors presented the highest $COD_{soluble}$ removal percentages. The E_h values presented an oscillation behavior at 10 cm depth (root zone) for planted reactors demonstrating the photosynthetic effect with illumination and darkness.

Keywords Biological reactors, artificial wetlands, oxidation-reduction potentials

Se realizaron experimentos a escala de laboratorio con sistemas de humedales artificiales para evaluar el rol que juegan los fenómenos de la difusión y la fotosíntesis usando como herramienta los potenciales de oxidación-reducción (E_h). Se emplearon cuatro reactores de laboratorio de 20 litros empacados con escoria volcánica. Se instalaron tres electrodos para medir los potenciales de oxidación-reducción a 2, 10 y 30 cm de la parte superior de los reactores y se registraron los valores usando un sistema de cómputo. Períodos de iluminación y oscuridad (16-8 h) se obtuvieron con lámparas que imitaban la luz solar. La eficiencia de depuración se midió en los influentes y efluentes de los reactores usando la demanda química de oxígeno soluble ($COD_{soluble}$). Se alimentó agua residual sintética preparándola diariamente disolviendo sacarosa, $(NH_4)_2SO_4$ y Na_3PO_4. Los resultados obtenidos indican que los fenómenos fotosintéticos tienen un efecto importante en la remoción de la demanda química de oxígeno soluble ($COD_{soluble}$), ya que los valores más altos de remoción se alcanzaron en aquellos que tenían hidrofitas. Los valores de E_h presentaron un comportamiento oscilante a 10 cm de profundidad (zona radicular) provocado por los períodos de iluminación y oscuridad.

Palabras clave Reactores biológicos, humedales artificiales o construidos, potenciales de oxidación-reducción

1. Introduction

Nowadays in Mexico, as in other emerging economies countries, around 80% of wastewater generated from different industrial activities is discharged to the receiving bodies without any previous treatment

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[1,2], resulting in a serious environmental and public health problem. Constructed or artificial wetlands (CW) or artificial wetlands (AW) represent a feasible alternative for such a problem since its low cost of maintenance and operation make them a very attractive technology from the economical and technical point of view since they perform very well in reducing water pollutants.

Constructed wetlands are based on the following fundamental principles: biochemical activity of microorganisms, the oxygen supply leaked from root plants, and a bed material who serves as a support for both microorganisms and plants, this material operate as a filter for many particles [3,4]. These elements eliminate dissolved and suspended substances in the wastewater and biodegrade the organic compounds towards its mineralization.

Artificial wetlands can be employed as a complementary system in the existing treatment plant [5] to improve water quality (polishing), and can also be used as the main treatment systems for small communities [6]. Studies regarding oxygen diffusion from atmosphere to the root zone [7,8]; photosynthetic oxygen provision [9], and those regarding convective oxygen supply in packed reactors [10], may help to evaluate these effects on pollutants depuration at experimental-scale or prototype-scale using oxide-reduction potentials.

Oxidation-reduction potentials (E_h) or redox conditions can be used as an indirect measurement of the anaerobic and aerobic conditions prevalent in the bulk of the wastewater treatment systems. This parameter can be linked to bulk oxygen content but, as it is not the only element that can modify it, some other considerations have to be made, such as the presence of aerobic bacteria.

Based on the above information, particularly the studies focused on oxygen diffusion to the root zone for both mechanisms, photosynthesis and the intermittent convective entrance of oxygen [9,10], lab-scale experiments were performed in order to study the pollutants transformation controlling phenomena, particularly the photosynthesis mechanism because oxygen coming through the root plants has an effect on oxidation-reduction (redox) conditions, and this effect remains in controversy [3].

Thus, the objectives of this research were to evaluate the oxidation-reduction potentials in the root zone of a reactor open to the atmosphere with one *Phragmites* shoot and to evaluate its ability to degrade dissolved chemical contaminants ($COD_{soluble}$) added to tap water using as controls three reactors (one with a *Phragmites* shoot covered to reduce air diffusion, and two more with the same characteristics but without plant).

2. Methodology

2.1 Laboratory-scale reactors

Four laboratory-scale reactors were constructed. The reactors consisted of plastic vessels, 30 cm diameter and 35 cm height. The reactors were filled completely with volcanic slag (*tezontle*, in Aztec language). One shoot of plant (*Phragmites australis*) was placed centrally inside two reactors (RA_1 and its replica without difussional oxygen RB_1). Both shoots were taken from the same mother plant and the other two reactors remained unplanted (RA_2 and its replica without diffusional oxygen RB_2), as control systems. Reactors RB_1 and RB_2 were closed with a plastic cover containing four holes through which the plant grew and the redox sensors were placed. Wastewater working volume was set to have flooding conditions to minimize the effect of convective oxygen transfer through air sucking [10]. Figures 1a and b show the complete experimental system used.

2.2 Experimental conditions

Synthetic wastewater was used for all reactors, and was daily prepared by dissolving sucrose, $(NH_4)_2SO_4$, and $Na_3PO_4.12H_2O$ in a 40L container with tap water, resulting in a C:N:P ratio of 15:1:0.1, and a soluble COD of 450 mgO_2/L which is a typical value for domestic effluents or sewage [11].

Fig. 1a Photograph of the system.

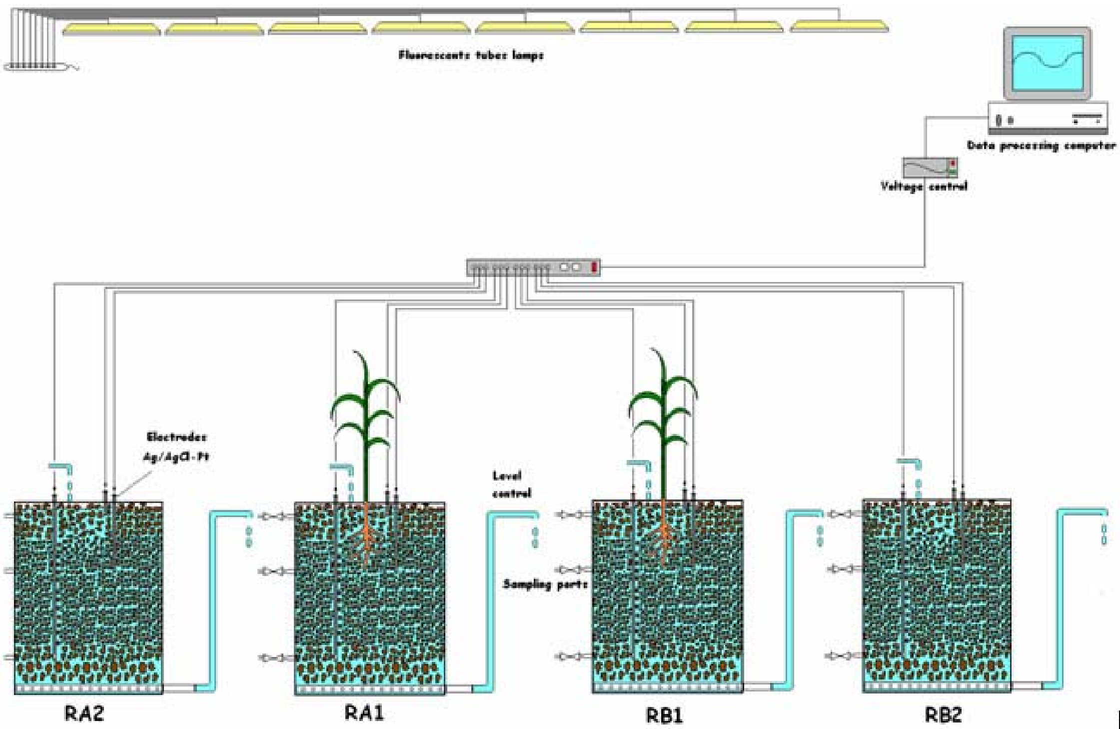

Fig. 1b Experimental system.

Daily inflow for each reactor was 7 L d^{-1} and hydraulic residence time considering porosity factor (51 %) was 1.8 days [12]. Reactors were kept flooded through a siphon system. They were placed in a controlled temperature room (22±2°C), illuminated with fluorescent tubes lamps (day light lamps) using a timer for 16 hours on and 8 hours off. After reactors reached steady state, E_h variations were measured by using commercial electrodes (Ag/AgCl-Pt), these electrodes were located at 2, 10 and 30 cm from top of each reactor. E_h values were recorded using a SEV software (Puebla, Mexico) in a personal computer. It was possible to record E_h (mV) values every 10 minutes, 24 hours a day. E_h electrodes were calibrated each 5 days in order to ensure representative measurements. $COD_{soluble}$ variations were measured using standard methodology [13], corrected by Oaxaca-Grande [14]. Both Eh and $COD_{soluble}$ values were measured during four weeks, in both illumination and darkness periods.

3. Results and discussion

3.1 Oxidation-reduction potentials (E_h)

Figure 2 shows the variations of the redox potentials for reactor RA_1 (planted and open to diffusive air) during the light and darkness periods (measurements correspond to four operating days in the steady state) at the three different reactor depths (2, 10, 30 cm). It is interesting to observe the oscillating pattern of this parameter at 10 cm depth, where the root zone is. This variation demonstrates that E_h is affected by the oxygen generated by the macrophyte during the illumination and darkness periods.

Another interesting phenomenon observed during these experiments is that E_h values are more negative than even those at 30cm deep. As this phenomenon takes place in both reactors that contain the plant (open and covered), it seems to be independent of the air oxygen that might be diffusing from the atmosphere as well as with the influent feed drops (Figure 3). The possible explanation lays on the fact that aerobic bacteria were found in this area and they are consuming the photosynthetic oxygen for degrading the dissolved pollutants (see Figure 6), and therefore, decreasing the E_h values even more than in the 30 cm deep area.

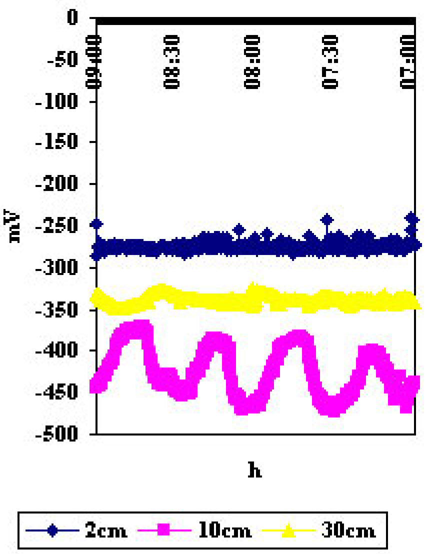

Fig. 2. Redox potentials variations (E_h) in reactor RA_1 (with plant and uncovered) during illumination and darkness periods.

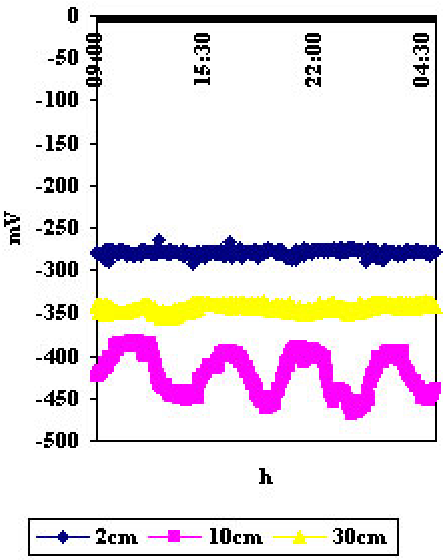

Fig. 3. Redox potentials variations (E_h) in reactor RB_1 (with plant and covered) during illumination and darkness periods.

It is important to consider that, in these two reactors, the plant has a very small root zone, and although photosynthetic oxygen is generated the amount is not enough to change the redox conditions near the electrode. The two reactors without plant, uncovered and covered, have a perfectly stratified pattern (Figures 4 and 5).

These aerobic bacteria seem to be consuming photosynthetic oxygen as they metabolize wastewater compounds, reducing overall $COD_{soluble}$ values (Figure 6), during the illumination period. This is confirmed with the darkness results, where removal is very similar to the control reactors without plant (no photosynthetic oxygen available), acting as sequencing reactors.

Figures 4 and 5 show the redox potentials at reactor RA_2 (unplanted and covered) .A homogeneous behavior was observed with a non oscillating pattern for both illumination and darkness periods as occurs for RA_1 and RB_1 since there is no photosynthetic oxygen generation.

These results suggest that oxygen entering with the influent drops undergoes a stratification (lower concentration at higher depth) and the concomitant stratification of E_h.

The pattern in RA_2 remained without change during illumination and darkness periods. This behavior is similar to that reported by some authors [15], where the change of E_h at different light intensities was studied.

E_h values at the surface (2 cm depth) of reactor RA_2 were less negative due to the presence of the oxygen contents at inflow wastewater drops that is transferred from atmosphere.

Conditions within reactor RB_2 were even more reductive than those for RA_1, RA_2, and RB_1.

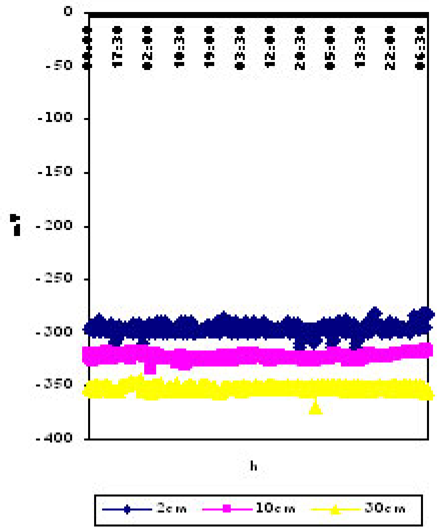

Fig. 4 Redox potentials variations (E_h) in reactor RA_2 (no plant and uncovered) during illumination and darkness periods.

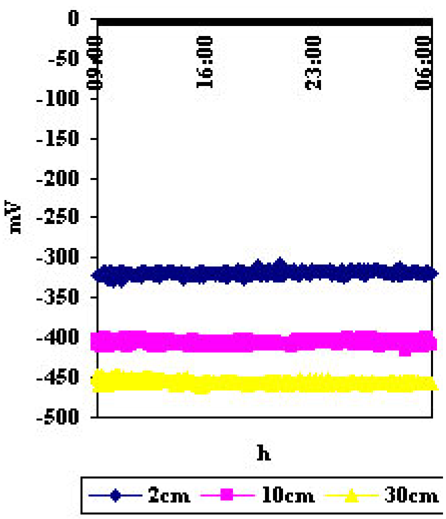

Fig. 5 Redox potentials variations (E_h) in reactor RB_2 (no plant and covered) during illumination and darkness periods.

3.2 Chemical oxygen demand values ($COD_{soluble}$)

Figures 6 and 7 show $COD_{soluble}$ values at the influent and effluent of the reactors and for both illumination and darkness periods.

Table 1 shows the overall percentages of $COD_{soluble}$ removals. These results clearly show a reduction of this parameter in the reactor (RA_1) and its three controls. The results were taken at the outlet of each reactor during the steady state for both illumination and darkness period. For illumination period it can be seen that reactor RA_1 (planted and uncovered) presented the highest COD removal (effluent $COD_{soluble}$ of 216.2 mg O_2/L), indicating that plant has an important effect in the reduction of $COD_{soluble}$. This effect lays on the fact that the root zone can serve as a support material for heterotrophic bacteria [3] which consume the oxygen that the plant supplies (photosynthetic and through aerenchyma -airy tissue found in roots of plants, which allows exchange of gases between the shoot and the root-), increasing degradation (Table 1).

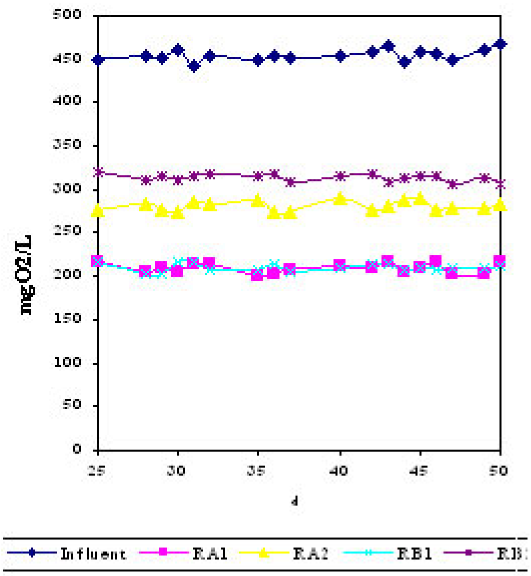

Fig. 6 Effluent $COD_{soluble}$ variations at steady state at for four reactors during illumination period.

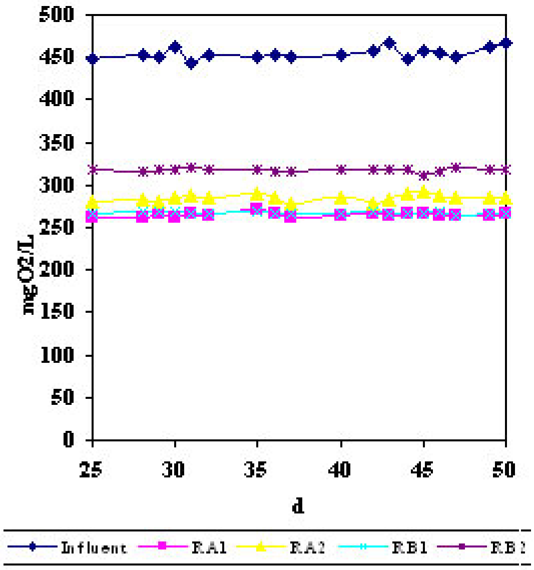

Fig. 7 Effluent $COD_{soluble}$ variations at steady state at for four reactors during darkness period.

Table 1 $COD_{soluble}$ Removal percentage for each reactor (steady state) during illumination and darkness periods.

Reactor	Illumination	Darkness
RA_1 (planted, uncovered, open to diffusive oxygen)	54.1	43.1
RB_1 (planted control, covered, closed to diffusive oxygen)	53.9	40.9
RA_2 (unplanted control, uncovered, open to diffusive oxygen)	39.8	38.7
RB_2 (unplanted control, closed to diffusive oxygen)	34.6	32.1

The $COD_{soluble}$ removal for control reactor RA_2 (unplanted and uncovered) was lower in comparison with RA_1 (effluent value of 281.4 mgO_2/L) due to the unplanted status. These outflow values are even lower that for control reactor RB_2, unplanted and covered (317.8 mgO_2/L) which suggest that diffusive transfer of oxygen exists within the inflow drops and this oxygen is being consumed at the first 2 cm.

$COD_{soluble}$ values for reactor RB_1 are very similar as those for RA_1 (211.44 mg O_2/L), suggesting that plant oxygen supply has the major effect in $COD_{soluble}$ reduction. Control reactor RB_2, which is the unplanted and uncovered control reactor, shows a lower $COD_{soluble}$ reduction efficiency in comparison with other reactors due to the fact that the only oxygen supply is the inflow oxygen contents.

It can be seen from Figure 7, that $COD_{soluble}$ values at the effluent of each reactor during dark periods are slightly higher than those for illumination period supporting the belief that photosynthesis is the controlling oxygen supply mechanism. $COD_{soluble}$ values in reactor RB_1 are similar to RA_1 values (265.88 mgO2/L) for darkness period which reinforce the fact that the atmosphere diffusive oxygen transfer to the reactor is very low and the effects on $COD_{soluble}$ removal are low too, during illumination period.

A small variation in reactors RA_2 and RB_2 was observed, because the oxygen transfer from atmosphere is consumed by heterotrophic bacteria lowering $COD_{soluble}$ (Table 2). Values for $COD_{soluble}$ at the outlet of reactors RA_2 and RB_2 were 284 and 319 mg O_2/L, respectively. In the case of reactor RB_2, no important variations were observed in $COD_{soluble}$ removal during both illumination and darkness periods due to the fact that there is no plant (as in RA_1or RB_1) that modifies the oxygen concentration.

Table 2 Number of colonies forming units per milliliter, CFU mL^{-1}, of heterotrophic bacteria (microaerobic and facultative bacteria) in the reactors effluent samples (steady state) (Factor 10^{-4}).

Reactor	2 cm	10 cm
RA_1 (planted, uncovered, open to diffusive oxygen)	2.95	4.70
RB_1 (planted control, covered, closed to diffusive oxygen)	2.00	4.00
RA_2 (unplanted control, uncovered, open to diffusive oxygen)	1.50	1.20
RB_2 (unplanted control, closed to diffusive oxygen)	0.95	0.71

4. Conclusions

As a conclusion, it can be said that the oxygen supplied by the plant to the root zone of the reactor and its control with plant (closed to diffusive oxygen) shows a greater effect in organic matter degradation than that transferred directly from atmosphere through diffusion.

From E_h results is possible to state that oxygen generated by plant is had the main effect on redox potentials variation and that under this specific experimental conditions, no important effect of atmospheric oxygen was observed.

Chemical oxygen demand removal was higher for planted reactors (uncovered RA_1 and covered RB_1) and these values were very similar (54.1, 43.1 and 53.9, 40.9 for illumination and darkness periods, respectively) suggesting that atmospheric oxygen had not an important effect on the elimination of this parameter.

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