Desalination and Water Treatment
www.deswater.com
doi: 10.1080/19443994.2015.1070292

57 (2016) 15125–15132
July

Taylor & Francis
Taylor & Francis Group

Enhanced bio-reduction of hexavalent chromium by an anaerobic consortium using henna plant biomass as electron donor and redox mediator

Jingang Huang[a,b], Mengke Wu[a], Junhong Tang[a,*], Rongbing Zhou[a], Jianjun Chen[a], Wei Han[a], Zhengmiao Xie[a]

[a]*Institute of Environmental Science and Engineering, College of Materials and Environmental Engineering, Hangzhou Dianzi University, Room S104, The 6th Building, Hangzhou 310018, P.R. China, emails: hjg@hdu.edu.cn (J. Huang), 526619708@qq.com (M. Wu), Tel./Fax: +86 571 86919158; emails: hjgah@163.com (J. Tang), zrb@hdu.edu.cn (R. Zhou), cjj_19@163.com (J. Chen), hanwei1982@hdu.edu.cn (W. Han), zhmxie@hdu.edu.cn (Z. Xie)*
[b]*State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, P.R. China*

Received 21 January 2015; Accepted 30 June 2015

ABSTRACT

The effects of henna (*Lawsonia inermis*) flower biomass on the enhanced bio-reduction of Cr(VI) were investigated in this study. The average Cr(VI) removal rate in the anaerobic system with the addition of henna flower powder achieved 2.04 mg L^{-1} h^{-1}, which was much higher than the rates in the activated sludge control, autoclaved sludge control, and adsorption control. Under anaerobic conditions, the organic compounds in henna flower powder could be leached out from the solid phase to the mixed solution, and then fermented to volatile fatty acids and H_2, acting as effective electron donors for the rapid bio-reduction of Cr(VI). The released and/or fixed lawsone not only shuttles electrons from the donor to the final acceptor of Cr(VI), but might also inversely improves the fermentation process of henna flower biomass.

Keywords: Hexavalent chromium; Henna plant biomass; Lawsone; Electron donor; Redox mediator

1. Introduction

Hexavalent chromium (Cr(VI)) linked compounds are widely used in industrial applications such as electroplating, tanning, textile dyeing, and wood treatment [1]. Due to the suspected carcinogenicity, toxicity, and environmental risks, Cr(VI) has been reported as one of the most hazardous heavy metals. Animals and humans which are exposed to Cr(VI) would suffer extracellular or intracellular damage. Cr(VI) can not only cause contact dermatitis and ulceration of the skin, but can also pass through cellular and nuclear membranes, and then strongly react with enzymes, chromosomal, and even DNA. Moreover, Cr(VI) is likely to be accumulated in the plant tissue and then enter the food chain, resulting in heavy ecological risks [2,3]. For these reasons, Cr(VI) is classified as a first class pollutant in China (GB 8978-1996), and its concentration is required to be below 0.5 mg L^{-1} before it can be discharged; and in the US State of California, the maximum Cr(VI) concentration in drinking water was limited to 10 μg L^{-1} [4]. Therefore, it always focuses on

*Corresponding author.

the removal of Cr(VI) from wastewaters to protect the living organisms in aquatic systems.

Due to the much lower toxicity, solubility, and permeability of trivalent chromium (Cr(III)) than Cr (VI), the reduction of Cr(VI) to Cr(III) and a subsequent precipitation via the formation of $Cr(OH)_3$ is an attractive option for engineering applications. These reduction processes include chemical and biological methods [5,6]. Under anaerobic conditions, soluble Cr (VI) can be reduced to Cr(III) first and then immobilized to the bacterial surface or accumulated intracellularly [7,8]. The former reductive process is the rate-limiting step.

Anaerobic bio-reduction of Cr(VI) is quite dependent on the availability of electron donors such as carbohydrates, organic acids, H_2, proteins, and alcohols [9–11]. These electron donors act as energy pools during the biological process. In addition, this bio-reductive process can be accelerated in the presence of redox mediators (RMs) such as anthraquinone-2,6-disulfonate, anthraquinone-2-sulfonate, 2-hydroxy-1,4-naphthoquinone (lawsone), 2-methyl-1,4-naphthoquinone (menadione), and humic acid [12–15]. Due to the easy washing off of the dissolved RMs in wastewater treatment systems, researchers have focused on the immobilization of RMs into special materials to avoid the its loss to the effluent [16,17]. However, the high cost of the immobilizing process still limits its widespread applications. Therefore, to overcome the low reduction rate of Cr(VI) and its high operational fee, researchers are trying to find effective and eco-friendly electron donors and RMs.

In recent years, many agricultural and forestial wastes, especially the raw and modified lignocellulosic materials, have been reported to effectively adsorb Cr (VI) on their surfaces [18,19]. Saha et al. have successfully use these inexpensive or cost-free, readily available materials such as mosambi (*Citrus limetta*) peel, mango leaves (*Mangifera indica*), and chatim tree (devil tree, *Alstonia scholaris*) saw dust to effectively adsorb Cr(VI) from contaminated water, with Cr(VI) adsorption capacity ranging from 250 to 333.33 mg g^{-1} [20–22]. In addition, plant biomass such as corncobs and cattails can serve as solid-phase electron donors and carbon sources for the bio-reduction of oxidized pollutants, such as nitrate and halogen-derivatives [23,24].

Henna plant (*Lawsonia inermis*) is cultivated worldwide that contains abundant lawsone, which is an effective RM capable of shuttling electrons from the primary donor to the final acceptor of Cr(VI) [25]. Therefore, apart from providing potential electron donors, natural henna plant biomass might also supply RMs simultaneously for the mediated Cr(VI) reduction in the anaerobic biological system. This study aimed to investigate the enhanced Cr(VI) removal with the addition of henna plant biomass, acting as a multiple role in supplying electron donors and RM.

2. Materials and methods

2.1. Chemicals and materials

Stocked Cr(VI) solution (10 g L^{-1}) was prepared by dissolving analytical grade potassium dichromate ($K_2Cr_2O_4$) in deionized water. All working solutions were prepared by diluting the stocked Cr(VI) with deionized water. Commercial henna plant biomass (flower) was purchased from Kaihangzhongyi Trading Co. Ltd, in Xinjiang, China. The flower was crushed to be able to pass through a 50 mesh sieve and then dried at 45°C for 10 h before use. The inoculated anaerobic sludge was obtained from a textile dyeing wastewater treatment plant in Zhejiang province, China. The sludge was washed three times with de-ionized water before adding to the serum bottles in this study.

2.2. Experimental set-up

Four 1,000 mL serum bottles were set up as the activated sludge control (B1), autoclaved sludge control (B2), adsorption control (B3), and reduction test (B4), respectively. B1 was cultured with active anaerobic sludge but without henna flower powder to assess the endogenous bio-reduction of Cr(VI) with decaying substrates as electron donors. The biological process of Cr(VI) removal in B2 and B3 was extinguished to investigate the adsorption of Cr(VI) by the inoculated sludge and/or the henna flower powder. B2 was amended with only autoclaved sludge (121°C, 0.12 MPa); whereas B3 contained both autoclaved sludge and dry-heat sterilized (135°C, 4.0 h) henna flower powder. In B4, henna flower powder (1.5 g L^{-1}) and active inoculated sludge were added to evaluate the bio-reduction of Cr(VI) with henna as a solid-phase electron donor and RM. After a complete removal of Cr(VI), adequate volume of stocked potassium dichromate solution (50 g L^{-1}) was once again added to B4 to recover the initial Cr(VI) concentration. This was conducted to investigate the Cr(VI) removal during the repeated batch.

The serum bottles were magnetically stirred at a temperature of 25 ± 1°C, and the initial pH in each system was adjusted to 7.0 ± 0.2 using $NaHCO_3$ buffer solution. In each bottle, the initial Cr(VI) concentration was 90 ± 10 mg L^{-1}, and the anaerobic

sludge was 1.28 g VSS L^{-1}. NH_4Cl (80 mg L^{-1}), KH_2PO_4 (20 mg L^{-1}), $MgCl_2{\cdot}6H_2O$ (20.3 mg L^{-1}), $CaCl_2{\cdot}2H_2O$ (14.7 mg L^{-1}), $FeSO_4{\cdot}7H_2O$ (2.8 mg L^{-1}), and stock trace metals and vitamins (1.0 mL/L) were all included in the serum bottles. All substances were prepared in N_2-flushed de-ionized water throughout the experiments.

2.3. Chemical analysis

Withdrawn mixture at appropriate time intervals, were firstly centrifuged at 4,000 × *g*, and then be filtered through 0.22-μm membrane filters. pH was measured by a portable pH/mV/temperature meter (HACH, sensION1, USA). The concentrations of Cr(VI) were determined by measuring the absorbance at 540 nm after reaction of Cr(VI) and 1,5-diphenylcarbohydrazide [26].

Volatile fatty acids (VFAs) and lawsone were both measured by high-performance liquid chromatography unit (HPLC, Agilent 1200, USA) equipped with an UV detector. VFAs were detected with a Shodex RSpak KC-811 analytical column following a Shodex RSpak KC-G guard column (Showa Denko, Japan) at 50°C. The mobile phase was phosphoric acid (H_3PO_4) solution (0.1%) at a flow rate of 0.7 mL min^{-1}, and the wave length was 210 nm. For lawsone analysis, an Agilent XDB-C18 column (4.6 × 150 mm, 5 μm) was employed at 35°C. The mobile phase was methanol: 0.05% H_3PO_4 (1:1) with a flow rate of 0.6 mL min^{-1}, and the wave length for detection was 278 nm.

Soluble chemical oxygen demand (SCOD) and volatile suspended solid (VSS) were determined according to Standard Methods [26]. To analyze the functional groups of henna flower biomass, a Nicolet 6700 FTIR spectrometer was used.

3. Results and discussion

3.1. Effect of henna plant biomass on Cr(VI) removal

The removal of Cr(VI) in the systems of activated sludge control (B1), autoclaved sludge control (B2), adsorption control (B3), and anaerobic reduction test (B4) are shown in Fig. 1. The decrease of Cr(VI) in B4 with inoculated anaerobic sludge and henna flower powder occurred much faster than those in the three controls (Fig. 1). Indeed, Cr(VI) was completely removed from B4 after 46 h, in the first operational batch; and then a reverting of initial Cr(VI) concentration at 94 h leaded to a ~60.5% removal of the added Cr(VI) in the following repeated batch. Nevertheless, by the end of the entire operational period (236 h), only 44.5, 19.6, and 35.4% of Cr(VI) removal was achieved in B1, B2, and B3, respectively.

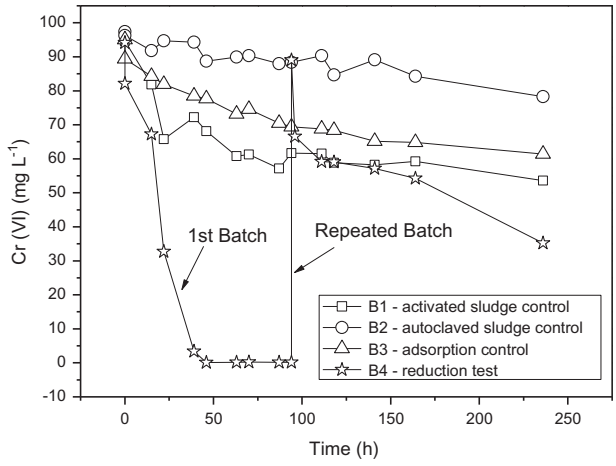

Fig. 1. The Cr(VI) concentrations within each designed batch in B1, B2, B3, and B4. The repeated batch was conducted in B4 after the complete removal of Cr(VI), when Cr(VI) was recovered to the initial concentration.

The activated sludge control (B1) shows a moderate removal of Cr(VI) with calculated average rate of 0.18 mg L^{-1} h^{-1}. This removal in B1 might be attributed to the adsorption of Cr(VI) by the sludge and/or the endogenous bio-reduction of Cr(VI) to Cr(III). These findings are in agreement with those of studies conducted by Han et al. [27] and Gardea-Torresdey et al. [28], who found that biosorption and bio-reduction were both involved in the Cr(VI) removal pathways in the culture of a microalgal isolate, *Chlorella miniata*. However, the removal of Cr(VI) in the autoclaved sludge control (B2) was the slowest, with a calculated average removal rate of 0.08 mg L^{-1} h^{-1}, implying a small contribution of Cr(VI) adsorption by sludge. The unbalanced removal rate between B1 and B2 was 0.1 mg L^{-1} h^{-1}, which might have been due to the endogenous bio-reduction of Cr(VI). In addition, the average Cr(VI) removal rate in the adsorption control test (B3) was 0.14 mg L^{-1} h^{-1}, including the adsorption by sludge and henna flower powder. Thus, the above results indicate that the average Cr(VI) removal rate of sludge adsorption, henna powder adsorption, and endogenous bio-reduction were 0.08, 0.06, and 0.10 mg L^{-1} h^{-1}, respectively. In R4, the average Cr(VI) removal rates in the first batch and the repeated batch were 2.04 and 0.38 mg L^{-1} h^{-1}, respectively. Although a previous study has reported that henna leaf-prepared carbon could act as an effective adsorbent for Cr(VI) removal under comparable initial concentrations in this experiment [29], the raw henna flower biomass in this study showed a relatively low contribution of adsorptive removal of Cr(VI). Therefore, the rapid decrease of Cr(VI) in R4 could

primarily be attributed to the bio-reduction of Cr(VI) to Cr(III). Subsequently, the accumulated Cr(III) precipitates on the bacterial surface might hinder the transfer of Cr(VI) across the cell membrane, resulting in a weakened Cr(VI) removal rate in the repeated batch (Fig. 1).

Under anaerobic conditions, the added henna flower powder, which is a solid-phase carbon source containing RMs, has the potential to provide electron donor, carbon source, and RMs simultaneously. This has been successfully established in our previous study of the enhanced bio-reduction of an azo dye Orange II upon the external addition of henna leaf biomass [30].

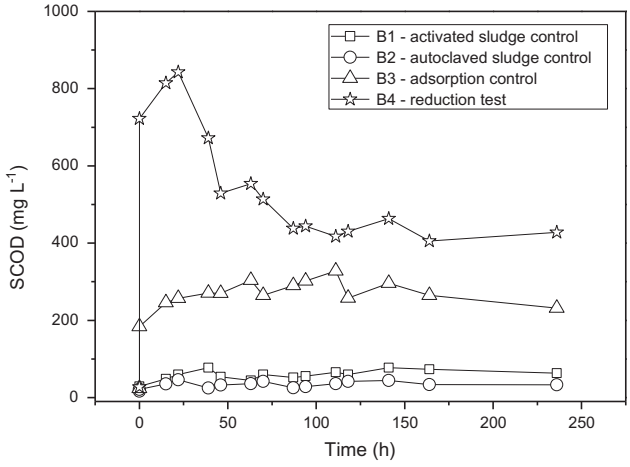

Fig. 2. The SCOD concentrations within each designed batch in B1, B2, B3, and B4.

3.2. Multiple roles of henna flower biomass

3.2.1. Electron donor source

Natural plant biomass is the most abundant carbon sink globally, and their main gradients are cellulose, hemi-cellulose, and lignocelluloses [31]. These materials can act as an inexpensive and widely available energy reservoirs for the bio-reduction of various contaminants [23,24,32]. Furthermore, Mukherjee et al. [33,34] have recently reported that the water extract of natural Sajina (*Moringa oleifera*) flower and Neem (*Azadirachta indica*) sawdust, which contain a variety of reducing components including sugar and amino acid, served as effective electron donors for the reduction of Cr(VI) to Cr(III) under acidic condition (pH 2). This process can be enhanced by the added surfactant such as sodium dodecyl sulfate. In this study, the reduction of Cr(VI) to Cr(III) in B4 was driven by the added microorganisms under nearly neutral pHs, with the released organic compounds as electron donor and lawsone as an RM, resulting in almost 100% removal of Cr(VI) after 46 h.

The results show that the SCOD in henna-free culture (B1 and B2) was lower than those in henna-added culture (R3 and R4) (Fig. 2). During the entire operational time in B1 and B2, the SCOD was limited to 70 mg L^{-1}. This low SCOD might be attributed to the decay of inoculated anaerobic sludge. Moreover, it is interesting that the SCOD concentration in B3 quickly increased to ~250 mg L^{-1} within 15 h, and further slightly increased to ~300 mg L^{-1} over the remainder of the experimental period, suggesting that the organic compounds can also be released from henna flower powder abiotically. These findings were supported by a previous study by Chen et al. [31], who found that carbohydrate could be abiotically released from the cattail litter. Due to the inactivation of biological processes in B3, this released carbohydrate would not be further fermented to VFAs and other intermediates. Therefore, the abiotically released SCOD in B3 might be composed of carbohydrates, proteins, and other labile organic compounds such as the leached lawsone.

In addition, the SCOD in the anaerobic reduction test (B4) was much higher than those in B1, B2, and B3. Moreover, it quickly increased to the maximum value of 842 mg L^{-1} within 22 h, then decreased with the ongoing operational time. At the end of the batch test (236 h), the net accumulation of SCOD was 427 mg L^{-1}. This decreased SCOD acted as electron donor for Cr(VI) removal, while also it may sink to the microorganism yield, H_2, and methane production. Therefore, the lower concentration level of SCOD (acting as an energy pool) in the repeated batch (after 94 h) might result in a weakened Cr(VI) removal process (Fig. 1). Henna powder could be firstly hydrolyzed to carbohydrates and proteins, then fermented to C_2–C_5 VFAs and H_2 by microorganisms under anaerobic conditions. These C_2–C_5 VFAs include acetate, propionate, butyrate, valerate, and their isomers. However, in this study, acetate was detected as the only constituent of VFAs in B4, and its maximum concentration was 69.6 mg L^{-1} at 22 h. Acetate is an intermediate during the fermentation process and was always found to be the main constitute of the produced VFAs during the fermentation of plant biomass such as cattail (*T. latifolia*) [31]. However, acetate can be utilized subsequently for methanation and Cr(VI) bio-reduction in anaerobic conditions. Therefore, the net acetate concentrations in B4 appear a wave-like variation and even depletion during different operational stages (Fig. 3). Furthermore, it was found that acetate was not

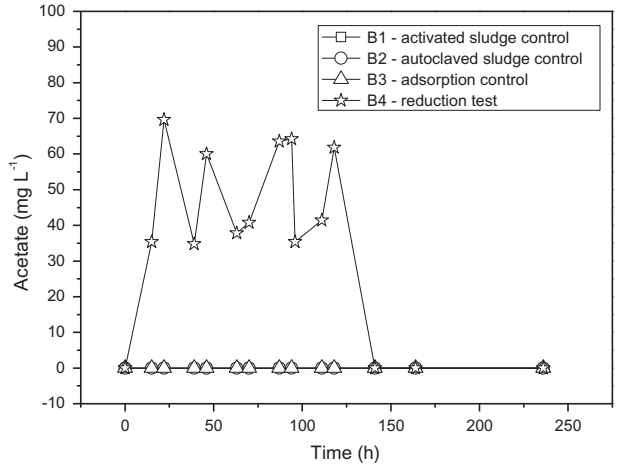

Fig. 3. The acetate concentrations within each designed batch in B1, B2, B3, and B4.

detected in any time of the three controls in B1, B2, and B3 (Fig. 3), indicating the absence of fermentation in these systems. This resulted in a relative lower pH in B4 than in the other controls (Fig. 4).

On the one hand, because acetate was a "final" VFA form and could no longer produce H_2, the higher acetate accumulation in B4 implied a higher H_2 production during the acetification of organic compounds derived from henna plant biomass. H_2 was an effective and direct electron donor for Cr(VI) reduction [14], therefore leading to enhanced reduction of Cr(VI) in B4. On the other hand, VFAs are also very effective for the bio-reduction of oxidized pollutants and can even replace H_2 as a direct electron donor for complete dechlorination [35]. Previous studies have identified that acetate was an effective electron donor for the bio-reduction of Cr(VI) [36,37] and could also serve as an effective electron donor for the enhanced bio-reduction of Cr(VI) in this study.

3.2.2. Redox mediator

RM can shuttle electrons from the primary donor to the final acceptor during the reduction of oxidized pollutants. The FTIR spectrum of henna flower powder (Fig. 5) shows two specific bands of transmission at 1,610 and 1,730 cm^{-1}, respectively, indicating the presence of 2-hydroxy-1,4-naphthoquinone (lawsone) [38]. Lawsone is a typical RM containing quinone group that has been proven to be an effective electron shuttling system for the mediated reduction of azo dyes, nitro-aromatic compounds, and halogen-derivatives [16]. Because the associated lawsone in henna flower powder might be leached out to the mixed solution, the available lawsone involved in the mediated Cr(VI) reduction in B4 could be present in both soluble and fixed state. As shown in Fig. 6, the soluble lawsone could be detected by the HPLC in the liquid phase of B3 and B4. Furthermore, it was noticed from Fig. 6 that the concentrations of soluble lawsone in B3 and B4 were at comparable levels, suggesting that soluble lawsone was abiotically released to the liquid phase from the henna flower powder. Soluble lawsone (35 mg L^{-1}) has been reported to enhance the Cr(VI) reduction by resting *Escherichia coli* cell using glucose as an electron donor [12].

Lawsone content in the henna plant biomass reached more than 1.8% [39]. However, at most times in this study, the soluble lawsone was below 5 mg L^{-1} upon the addition of 1.5 g L^{-1} of henna powder

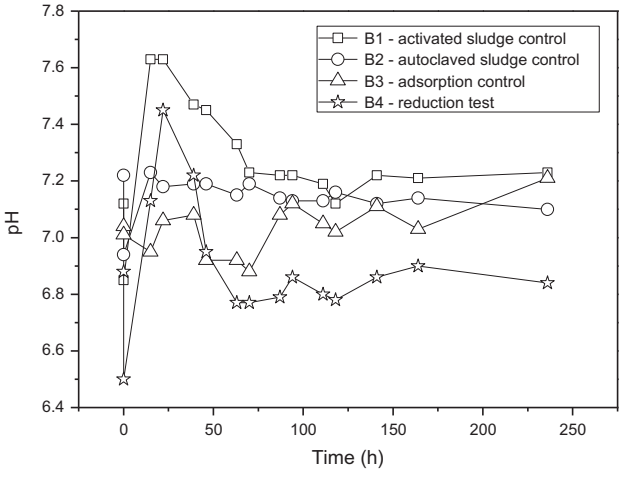

Fig. 4. The variation of pHs within each designed batch in B1, B2, B3, and B4.

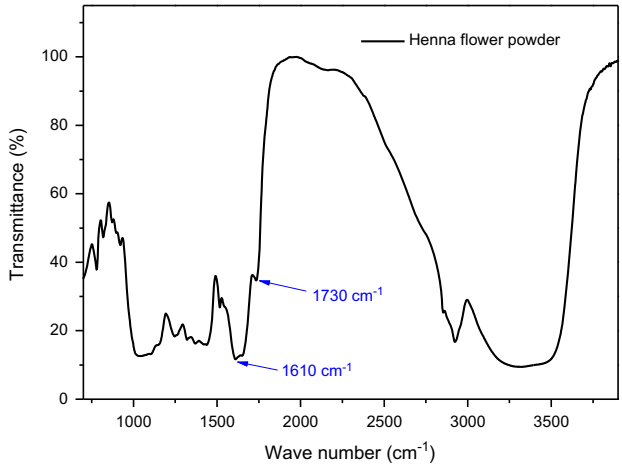

Fig. 5. FTIR spectra of the raw henna flower powder.

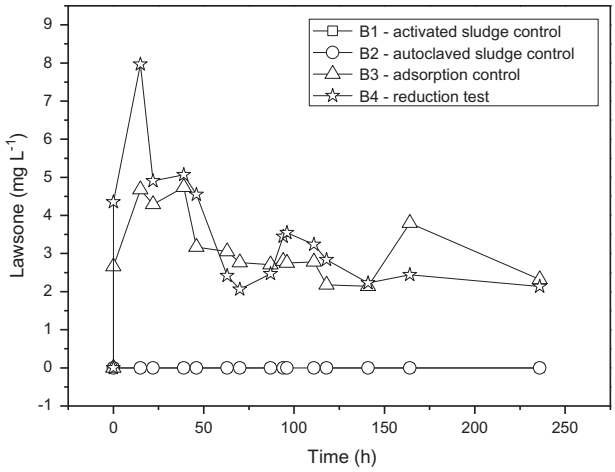

Fig. 6. The soluble lawsone concentrations within each designed batch in B1, B2, B3, and B4.

(Fig. 6), suggesting that only part of the associated lawsone was released to the solution. Thus, both the soluble and fixed lawsone could contribute to the mediated bio-reduction of Cr(VI) in B4.

In addition, it was also recently reported that quinone-based RMs including lawsone can promote the fermentation process, enhancing the production of VFAs and H_2 [40,41]. This process might introduce effective electron donors for Cr(VI) reduction in this study.

3.2.3. Future outlook

Henna plant biomass is a natural, inexpensive, and widely available lignocellulosic resource found worldwide. Under anaerobic conditions, henna plant biomass can simultaneously provide electron donors and RM (lawsone) for the effective bio-reduction of Cr(VI). This will improve the removal of Cr(VI) in the wastewater and reduce the operational costs. However, there are still some issues to be addressed. For example, the addition of henna plant biomass should be dependent on the Cr(VI) load of the wastewater and controlled at a minimum dosage to avoid the loss of organic compounds and potential secondary pollution. Additionally, the effects of lawsone on the production of intermediates during the fermentation process and the effects of this intermediate products on Cr(VI) reduction require further investigation.

4. Conclusions

The average Cr(VI) removal rate in the anaerobic reduction system with the addition of henna flower achieved 2.04 mg L^{-1} h^{-1}, which was much higher than those in the activated sludge control, autoclaved sludge control, and adsorption control. The bio-reduction was one of the main pathways to Cr(VI) removal in the anaerobic reduction system. Under these conditions, natural henna flower biomass played multiple roles in providing electron donors and RM (lawsone) for the enhanced bio-reduction of Cr(VI). Although organic compounds such as carbohydrates could be leached out to the solution, fermentative products such as VFAs and H_2 were the effective electron donors for the rapid bio-reduction of Cr(VI). Overall, the results of this study provide new insight into the removal of Cr(VI).

Acknowledgments

This research was supported by the Foundation of the State Key Laboratory of Pollution Control and Resource Reuse, China (No. PCRRF13013), the Research Foundation of Educational Commission of Zhejiang Province of China (No. Y201430800), the National Science Foundation of China (No. 51408171), and the National Science Foundation of China (No. 41373121).

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