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ORIGINAL PAPER

Bacteria-immobilized electrospun fibrous polymeric webs for hexavalent chromium remediation in water

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Abstract The development of hexavalent chromium remediating fibrous biocomposite mats through the immobilization of a hexavalent chromium reducing bacterial strain, *Morganella morganii* STB5, on the surfaces of electrospun polystyrene and polysulfone webs is described. The bacteria-immobilized biocomposite webs have shown removal yields of 93.60 and 93.79 % for 10 mg/L, 99.47 and 90.78 % for 15 mg/L and 70.41 and 68.27 % for 25 mg/L of initial hexavalent chromium within 72 h, respectively, and could be reused for at least five cycles. Storage test results indicate that the biocomposite mats can be stored without losing their bioremoval capacities. Scanning electron microscopy images of the biocomposite webs demonstrate that biofilms of *M. morganii* STB5 adhere strongly to the fibrous polymeric surfaces and are retained after repeated cycles of use. Overall, the results suggest that reusable bacteria-immobilized fibrous biocomposite webs might be applicable for continuous hexavalent chromium remediation in water systems.

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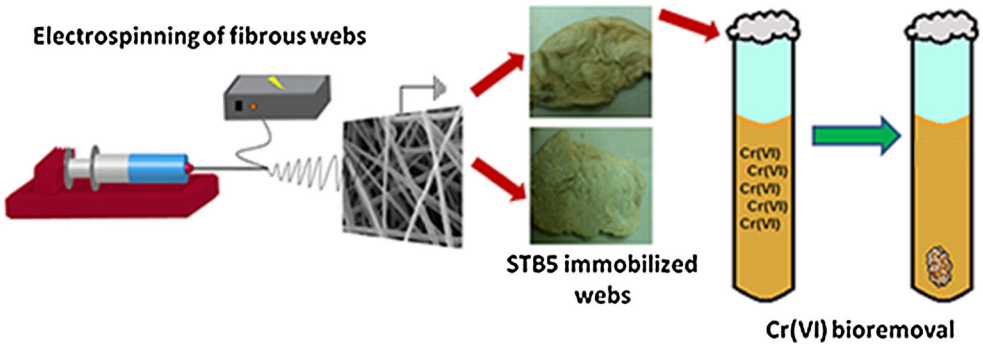
Graphical Abstract



Keywords Bioremoval · Electrospinning · Polystyrene · Polysulfone

Introduction

Chromium is a commercially important metallic element that is integral for many important industrial processes, such as electroplating, steel production, leather tanning, textile manufacturing and chromate preparation (Quintelas et al. 2009). The trivalent (Cr(III)) and hexavalent (Cr(VI)) forms are the most commonly encountered forms in nature (Bankar et al. 2009). While Cr(III) is not transported into cells and can be tolerated by many organisms at moderate concentrations, Cr(VI) is a toxic and carcinogenic form that readily permeates through biological membranes and may disrupt the functions of intracellular proteins and nucleic acids (Kilic and Donmez 2008). Chromium has been designated as a major pollutant by the United States Environmental Protection Agency (US EPA), and the legal limit defined for all forms of chromium, including Cr(VI), in drinking water is 0.1 mg/L (US EPA 2010). Heavy metal contamination in water systems can be treated by physical or chemical treatment methods (e.g., chemical oxidation or reduction, ion exchange, reverse osmosis) (Zahoor and Rehman 2009). However, there are several problems related with these techniques such as high operating and maintenance costs, high energy requirements, operational complexity and the production of secondary waste products (Mishra and Doble 2008). Today, biological treatment methods have received considerable attention as potential alternatives to conventional treatment methods (Mishra and Doble 2008; Quintelas et al. 2008; Al-Gheethi et al. 2014). In general, bioremediation of heavy metals is performed under acidic pH, since the existence of excess hydrogen ions in the medium facilitates the reduction of metal cations, resulting in higher removal efficiencies (Ergul-Ulger et al. 2014). However, these are not self-sustaining and require the constant influx of externally produced biomass, as most microorganisms cannot tolerate acidic environments and perish rapidly under such conditions. In addition, the water system must be further treated for neutralization before discharge. For that reason, bioremediation at neutral conditions with living microorganisms is a more eco-friendly process and allows metal removal to occur continuously without external intervention. *Morganella morganii* STB5 is a bacterial strain previously isolated for this purpose and can be used for the effective removal of Cr(VI) at neutral conditions.

Carrier materials can be used to enhance the heavy metal removal capacities of bioremediative organisms (Yang et al. 2009). Electrospun nanofibers are popular choices as carrier materials, and they have already been studied for pollutant removal (Chauhan et al. 2014; Xu et al. 2015). Polystyrene (PS) and polysulfone (PSU) are two common biocompatible polymers (Pinchuk 1989) that have been used for water filtration, and there are various examples in the literature about the applications of these polymers as electrospun nanofibers for filtering purposes (Gopal et al. 2007; Roso et al. 2008; Uyar et al. 2009, 2010). Studies regarding the use of microorganism-integrated electrospun fibrous biocomposites for pollutant removal have recently begun to appear in the literature (Klein et al. 2009; Eroglu et al. 2012; Klein et al. 2012; Sarioglu et al. 2013; San et al. 2014; San-Keskin et al. 2015a, b; Sarioglu et al. 2015). Lower space and growth medium requirements, ease of handling and potential reusability of these systems are some of the main advantages for using them in remediation studies (Eroglu et al. 2012). Immobilization of microorganisms on a carrier matrix protects them from harsh environmental conditions and stresses associated with heavy metal toxicity (Hall-Stoodley et al. 2004). In addition, natural adhesion of bacteria permits the formation of biofilms and maximizes cell viability and biochemical activity (Liu et al. 2012).

In this study, development of two novel biocomposite materials for Cr(VI) removal in water by immobilization of

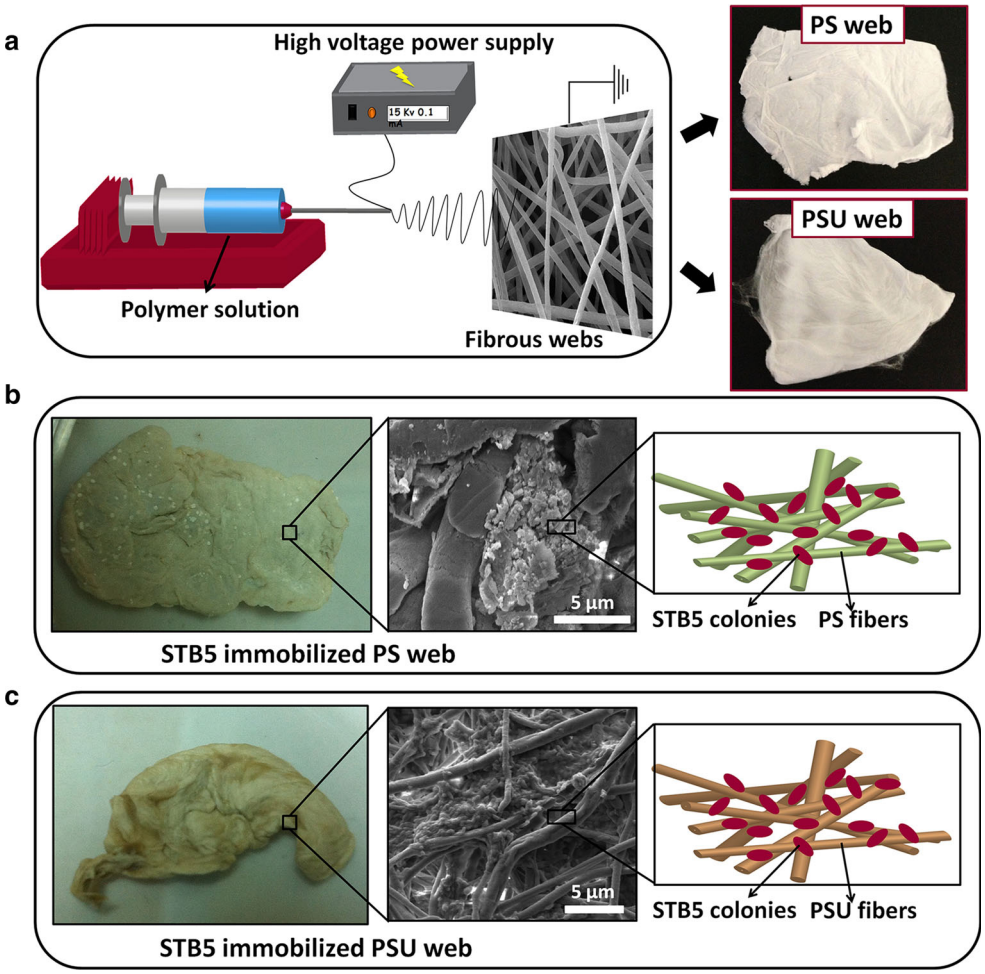


Fig. 1 **a** Schematic representation of electrospinning process and photographs of PS and PSU webs, **b** photographs of STB5-immobilized PS and **c** STB5-immobilized PSU webs along with SEM micrographs and schematic representations of bacterial cells on fibrous surfaces

a previously isolated *Morganella morganii* STB5 strain on electrospun PS and PSU fibrous webs is described. Integration of PS and PSU webs with bacterial cells is aimed to be effective for continuous Cr(VI) remediation in aqueous systems. This study was carried out in Ankara, Turkey, between the years 2014 and 2016.

Materials and methods

Electrospinning of PS and PSU webs

The homogenous electrospinning solution was prepared by dissolving 30 % (w/v) polystyrene (PS, Mw ~208,000, Sigma-Aldrich) in *N*,*N*-dimethylformamide (DMF, anhydrous, 99.8 %, Sigma-Aldrich) or 32 % (w/v) polysulfone (PSU, Mw ~60,000, Scientific Polymer Products, Inc.) in *N*,*N*-dimethylacetamide/acetone (9/1, (v/v)) (DMAC, Sigma-Aldrich, 99 %; acetone, Sigma-Aldrich, ≥99 % (GC) binary solvent mixture. Each polymer solution was loaded in a syringe with an inner diameter of 0.4 mm. The syringe was fixed horizontally to the syringe pump (model KDS-101, KD Scientific, USA). The electrode of the high-voltage power supply (Spellman, SL30, USA) was clamped to the metal needle tip, and the plate aluminum collector was grounded. Electrospinning parameters were adjusted as follows: feed rate of solutions = 0.5 mL/h, applied voltage = 10 kV, tip-to-collector distance = 10 cm. Electrospun nanofibers were deposited on a grounded stationary plate metal collector covered with aluminum foil. The electrospinning apparatus was enclosed in a Plexiglas box, and electrospinning was performed at 25 °C at 20 % relative humidity. Collected nanofibers/nanowebs were dried in vacuum oven at 50 °C overnight to remove residual solvent. The electrospinning process is schematically represented in Fig. 1.

Contact angle measurements

Thin surfaces of PS and PSU webs were electrospun on microscope slides to be analyzed with a contact angle measurement system (Dataphysis, OCA 30). Contact

angles were measured over a relatively intact and smooth region for each web; three independent measurements were recorded for each sample. Measurements were performed in a closed chamber at ambient temperature.

Growth and immobilization of *Morganella morganii* STB5

The bacterial strain (*Morganella morganii* STB5) utilized in this study was previously isolated from a local river (Ankara River). Bacterial immobilization was achieved by the inclusion of PS or PSU webs in the growth media of newly inoculated bacteria. Bacterial colonies were maintained for 30 days in 100-mL Erlenmeyer flasks containing M1 growth medium (pH 7.0). The ingredients of M1 growth medium are: 10 g/L peptone, 2 g/L meat extract, 1 g/L yeast extract and 5 g/L NaCl (≥99 %) in distilled water. After 30 days of incubation, bacterial immobilization was confirmed by scanning electron microscopy (SEM) analysis. Following confirmation of bacterial immobilization, bacteria-immobilized PS and PSU web samples of equal weights were prepared for Cr(VI) bioremoval experiments. All reagents utilized were purchased from Sigma-Aldrich (USA).

Cr(VI) bioremoval by using STB5/PS and STB5/PSU biocomposite webs

M1 growth medium was used in the Cr(VI) bioremoval studies, and all tests were performed in triplicate. The bacterial growth media were spiked with different amounts of Cr(VI) (10, 15 and 25 mg/L, in the form of $K_2Cr_2O_7$, ≥99 %, Sigma-Aldrich) and inoculated with free bacterial cells, bacteria-free fibers or bacteria-immobilized fibers prior to incubation at 150 rpm and 30 °C for 72 h. The positive control contained free bacterial cells ($\sim 10^8$ cfu/mL), the negative control contained pristine fibers, and the experimental samples contained bacteria-immobilized PS or PSU fibers, where the w/v ratio of web samples was fixed as 2.8 mg/mL. Samples were collected periodically to determine the remaining amount of Cr(VI). Cr(VI) concentrations were measured via 1,5-diphenylcarbazide, following the EPA protocol (US EPA 1992) for hexavalent chromium detection. The removal capacities (Q_{eq}) of free STB5 cells and STB5-immobilized web samples were calculated by Eq. (1)

$$Q_{eq}(\text{mg/g}) = (C_0 - C_f) \cdot V/M \quad (1)$$

where C_0 is the initial Cr(VI) concentration (mg/L), C_f is the final Cr(VI) concentration (mg/L), V is the solution volume (L), and M is the total bacterial cell biomass (g) at equilibrium (Buchko et al. 1999).

As demonstrated previously, *Morganella morganii* STB5 cells do not store or accumulate Cr(VI) without conversion, as no Cr(VI) release could be observed following the destruction of bacterial cell membranes through sonication (Ergul-Ulger et al. 2014). It was therefore assumed that all decreases in Cr(VI) concentrations are due to reduction and the removed Cr(VI) is reduced entirely to the stable Cr(III).

Adsorption isotherms and kinetics studies

Adsorption isotherm coefficients were determined upon three isotherm models (Langmuir, Freundlich and Toth) using the isotherm parameter fitting software IsoFit (Wagner et al. 2005). The order of reactions for Cr(VI) removal was predicted by plotting zero-, first-, second- and third-order plots of STB5/PS and STB5/PSU webs to calculate and compare their R^2 values for evaluation of the best fitting models.

Scanning electron microscopy (SEM)

Millimeter-length PS and PSU webs with and without bacterial immobilization were cut and prepared for SEM analysis to evaluate bacterial attachment before and after Cr(VI) bioremoval experiments. A modified protocol was utilized for SEM sample fixation (Greif et al. 2010). Briefly, samples were washed twice with PBS (phosphate-buffered saline) buffer and incubated overnight in 2.5 % glutaraldehyde solution (prepared in PBS buffer) at room temperature. Samples were then washed twice by PBS buffer and dehydrated by immersion in a series of ethanol–water solutions (30–96 %). All fixed samples were coated with 5 nm Au–Pd prior to SEM imaging (Quanta 200 FEG SEM, FEI Instruments, USA).

Reusability and post-storage performances of STB5/PS and STB5/PSU fibrous biocomposites

Cr(VI) bioremoval studies were performed five times to evaluate the reusability of STB5/PS and STB5/PSU fibrous biocomposites. Prior to each cycle, biocomposites were washed with PBS buffer twice and then incubated overnight in this buffer to eliminate any unattached bacteria. Cr(VI) bioremoval experiments were performed with the parameters as described above (incubation at 150 rpm and 30 °C for 72 h). The initial Cr(VI) concentration was fixed at 25 mg/L, the remaining Cr(VI) concentrations were measured at 0 and 72 h, and the percentile removal of Cr(VI) was calculated using these results. Each cycle was ended after 72 h of incubation, and washing steps were repeated for each biocomposite before starting the next cycle. All tests were done in triplicate.

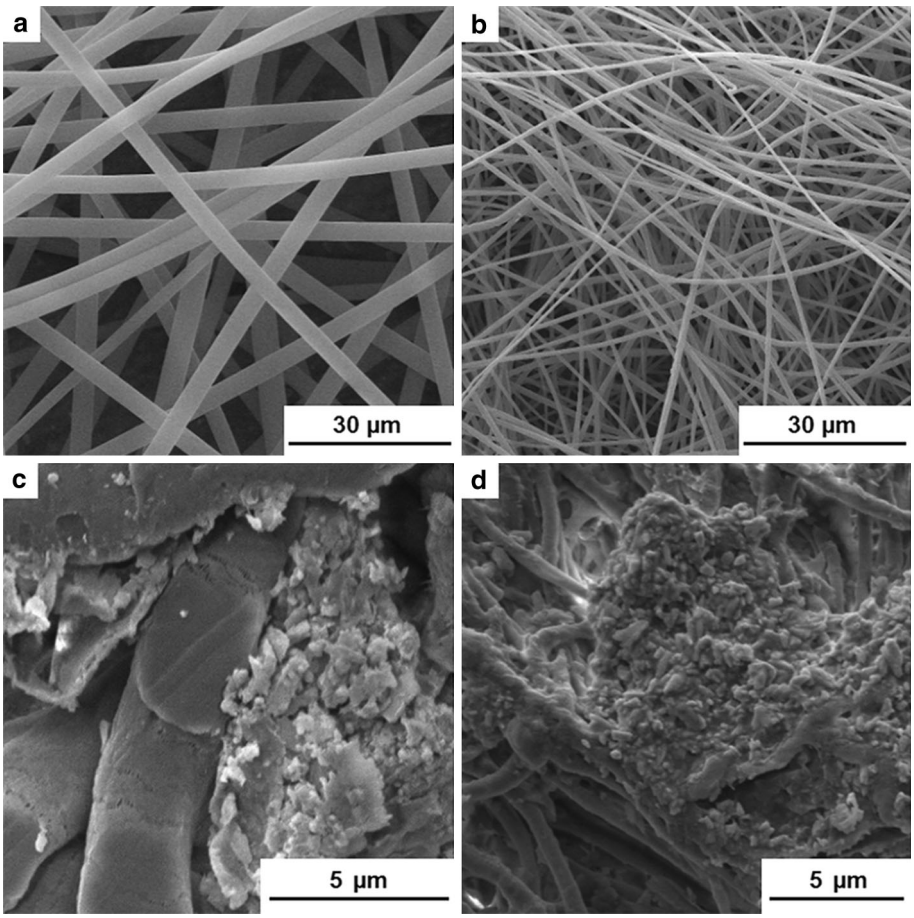


Fig. 2 SEM micrographs of **a** PS and **b** PSU webs without bacterial immobilization, and **c** STB5-immobilized PS and **d** STB5-immobilized PSU webs after 30 days of incubation for bacterial immobilization

Results and discussion

Attachment of bacterial cells on PS and PSU webs

Polystyrene (PS)- and polysulfone (PSU)-based polymeric materials can be used for water purification as membranes or filters, and there are several reports in the literature about the applications of these polymers as electrospun nanofibers for water filtering purposes (Gopal et al. 2007; Roso et al. 2008; Uyar et al. 2009, 2010). In this study, high-surface area electrospun PS and PSU fibers were used as substrates for bacterial attachment and the combined system was subsequently utilized for Cr(VI) removal. SEM analysis was performed to assess the extent of bacterial attachment on the fibrous surfaces, and an incubation period of 30 days was found to be required for robust bacterial adhesion. SEM images of PS and PSU webs before bacterial adhesion are shown in Fig. 2a, b. The average diameters of PS and PSU fibers were found as 2 μm and 0.8 μm, respectively. Furthermore, both electrospun webs were tested for hydrophobicity differences by contact angle (CA) measurements. PS webs were found to be relatively more hydrophobic (CA: 146.13° ± 4.74) compared to PSU webs (CA: 126.5° ± 5.91), although both webs have hydrophobic character. Figure 2c, d show that bacterial cells attached strongly on PS and PSU fibrous surfaces after 30 days of incubation, suggesting that both webs are suitable for strong bacterial adhesion. The bacterial cells formed biofilm structures by adhering to each other and to the surrounding PS and PSU fibers. Bacterial adhesion at this stage was found to be sufficient for further studies, and Cr(VI) bioremoval experiments were started with bacteria-immobilized PS and PSU webs.

Cr(VI) bioremoval capability of STB5/PS and STB5/PSU biocomposite webs

Initially, free STB5 cells were tested for Cr(VI) removal at five different pH levels to find out the optimal pH level for the removal process (Fig. 3a). Neutral pH (pH 7.0) was found as the optimal level for Cr(VI) remediation by STB5 cells, and the pH levels of further studies were adjusted accordingly. Since the highest Cr(VI) removal performance was achieved at neutral conditions instead of acidic environments, it was inferred that biological removal rather than adsorption is the primary removal practice for STB5

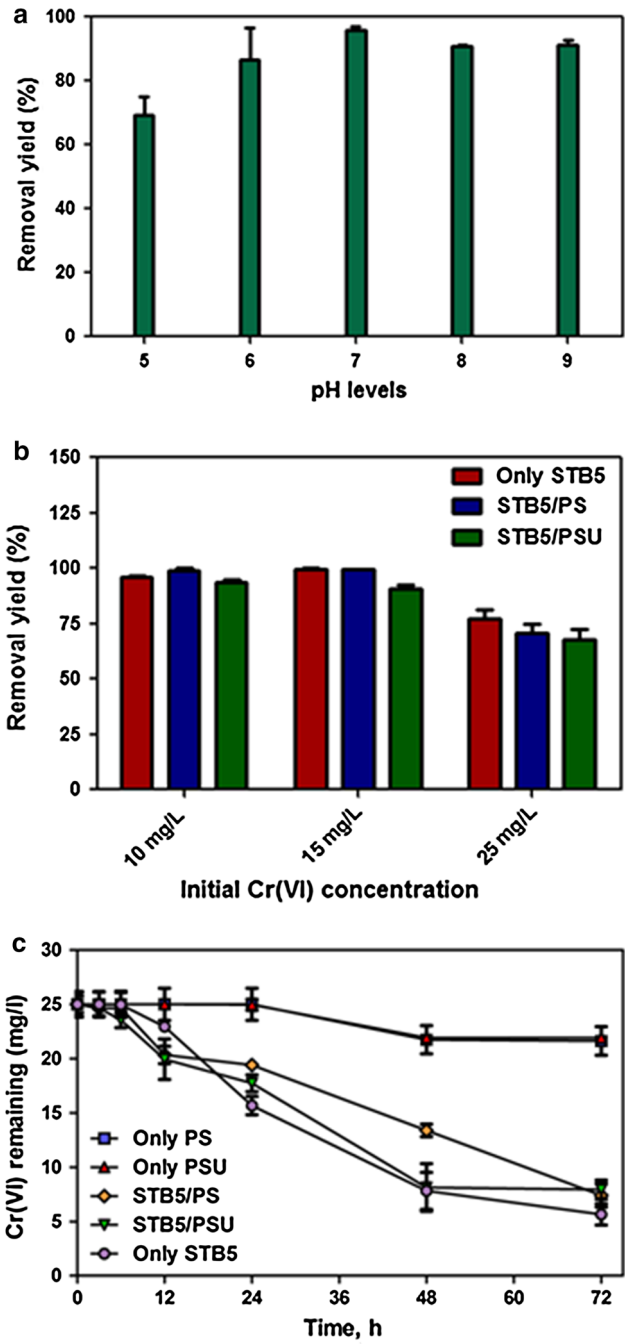


Fig. 3 Cr(VI) bioremoval profiles of **a** free STB5 cells at different pH levels, **b** only STB5, STB5/PS and STB5/PSU samples at different initial Cr(VI) concentrations and **c** only STB5, only PS, only PSU, STB5/PS and STB5/PSU samples at an initial concentration of 25 mg/L. *Error bars* represent mean of three independent replicates

cells. STB5/PS and STB5/PSU biocomposite webs have shown efficient removal of Cr(VI) at three different initial concentrations (10, 15 and 25 mg/L) within 72 h, and their Cr(VI) removal profiles are comparable to free bacterial cells, suggesting that the biocomposites can remediate Cr(VI) as effectively as freely floating cells and the results are highly promising for further Cr(VI) remediation studies (Fig. 3b). Bacteria-free PS and PSU webs have shown very similar and slight decreases (13.5 and 12.3 %, respectively) in the initial Cr(VI) concentration (Fig. 3c), possibly due to adsorption, implying that the Cr(VI) remediation capability of STB5/PS and STB5/PSU biocomposites is primarily due to the presence of bacterial cells. As demonstrated in Table 1, the Q_{eq} (removal capacity at equilibrium) values of free STB5 cells are always higher than STB5/PS and STB5/PSU webs, while Q_{eq} values of STB5/PS are following this sample generally. Two different types of polymeric webs were utilized as carrier matrices for bacterial immobilization, and PS was found to be a slightly better carrier matrix in terms of Cr(VI) removal capacity of its bacteria-immobilized form, possibly due to its more hydrophobic nature. It is known that gram-negative bacteria including *Morganella morganii* have hydrophobic surfaces because of the high lipid content on their cell walls, and hydrophobic bacteria have a preference to adhere on hydrophobic surfaces via hydrophobic interactions (Kochkodan et al. 2008; Giaouris et al. 2009). Therefore, hydrophobicity differences might play an important role on the adhesion of STB5 cells, and higher bacterial immobilization on PS web surfaces contributed to higher Cr(VI) removal performances by STB5/PS samples. Nonetheless, considerable amounts of Cr(VI) were removed in all experiments, suggesting that both biocomposites are promising candidates as supportive systems for conventional Cr(VI) remediation techniques. Since the biocomposites can work under non-acid-treated environments, such type of remediation can be applied in natural environments and allows the continuity of the remediation process.

Evaluation of adsorption isotherm coefficients and reaction kinetics

Adsorption isotherm plots for three different tested models (Langmuir, Freundlich and Toth) are presented in Fig. S1, and adsorption isotherm coefficients with their estimated values are listed in Table S1. While STB5/PSU fits well to each of the tested models, only STB5 and STB5/PS samples do not fit to any of the tested models, and thus the adsorption isotherm coefficients of these samples were not discussed. It was concluded that biological removal has the leading role in Cr(VI) remediation by free or immobilized bacteria, since adsorption isotherm coefficients fit only in one sample and the removal process performs best at neutral conditions where biological processes and enzymatic activity are more active usually. The highest correlation was observed in Langmuir model for STB5/PSU sample with the Ry^2 value of 0.997, suggesting that the dye removal process might be homogenous and monolayeric

Table 1 Removal capacities of only STB5, STB5/PS and STB5/PSU samples at equilibrium under different initial Cr(VI) concentrations, measured at the end of the 72 h removal period

Sample name	Initial concentration (C_0) (mg/L)	Removed Cr(VI) amount (mg/L)	Q_{eq} (mg/g)	Removal (%)
Only STB5	10	9.56	64.83 ± 5.68	95.8
STB5/PS	10	9.36	63.49 ± 4.3	93.6
STB5/PSU	10	9.39	63.64 ± 7.59	93.79
Only STB5	15	14.95	101.35 ± 14.5	99.56
STB5/PS	15	14.91	101.11 ± 15.3	99.47
STB5/PSU	15	12.52	84.9 ± 4.2	90.78
Only STB5	25	19.35	131.2 ± 12.4	77.41
STB5/PS	25	17.60	119.3 ± 7.65	70.41
STB5/PSU	25	17.07	115.7 ± 11.2	68.27

$T = 30$ °C, agitation rate: 150 rpm, average bacterial biomass concentration 0.15 ± 0.03 g/L

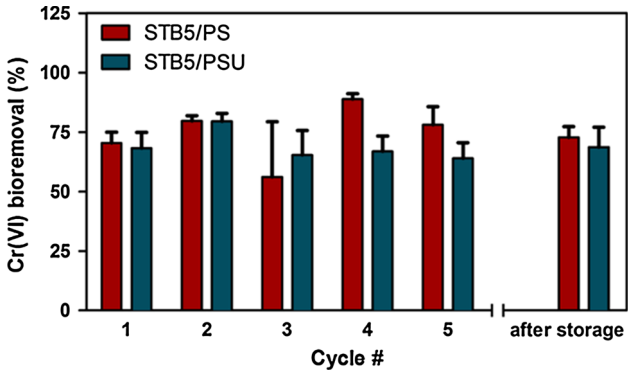


Fig. 4 Reusability and post-storage test results of STB5/PS and STB5/PSU biocomposite webs for an initial concentration of 25 mg/L. *Error bars* represent mean of three independent replicates

for this sample (Ergul-Ulger et al. 2014). The maximum removal capacity (Q_{max}) of STB5/PSU was measured as 139.83 mg/g under this model.

According to the reaction kinetics studies, it was observed that while STB5/PS fits better for zero-order reactions, only STB5 and STB5/PSU samples fit better for first-order reactions (Table S1). It has been reported that while enzyme-catalyzed reactions often fall under the zero-order mechanism (Tinoco et al. 1996), Cr(VI) reduction kinetics can fit under the first-order model (Lugo-Lugo et al. 2010), as previously observed by another bacteria-immobilized PSU web sample (San-Keskin et al. 2015a, b).

Reusability and applicability of STB5/PS and STB5/PSU biocomposites

The potential of long-term Cr(VI) removal with STB5/PS and STB5/PSU biocomposites was evaluated through a reuse test where the materials were washed and used for Cr(VI) removal in five consecutive cycles. Figure 4 shows the performance values of each cycle and the post-storage performances of both biocomposites following 15 days of storage at 4 °C in a closed moist environment. At the end of the reusability test, an average removal capacity of 74.63 % was achieved for STB5/PS, while this value was 63.95 % for STB5/PSU, indicating that both biocomposites retain their Cr(VI) removal capacity, and the STB5/PS biocomposite was relatively more efficient for continual Cr(VI) bioremoval. The results of the post-storage experiment were also promising, as 72.79 and 68.65 % Cr(VI) removal was observed for STB5/PS and STB5/PSU following 15 days of storage, demonstrating that both biocomposites can be stored for short periods of time without losing their Cr(VI) removal capabilities. These results as a whole are very promising and after process optimization, STB5/PS and STB5/PSU biocomposites may be utilized repeatedly for Cr(VI) removal and can be stored for longer periods of time, thus serving as reusable and storable materials for the remediation of Cr(VI) from aqueous environments. Following reusability and storage tests, the biocomposites were washed several times with PBS buffer and fixed for SEM analysis. Figure 5 shows bacterial biofilms are present on both PS and PSU webs, indicating that bacterial cells survive throughout the reusability experiments. It can be inferred that washing and reuse of bacteria-immobilized PS and PSU web samples did not lead to a viable decrease in the quantity of bacterial biofilms, and the bacterial cells are likely to be preserved on both PS and PSU webs.

Heavy metal remediation of aquatic systems is a substantial issue, and greener approaches are becoming more popular as of late (Flathman and Lanza 1998; Mulligan et al. 2001; Davis et al. 2003; Gavrilescu 2004; Congeevaram et al. 2007). In this study, a Cr(VI)-reducing bacterial strain was immobilized on electrospun PS and PSU webs, and Cr(VI) removal performances of these newly

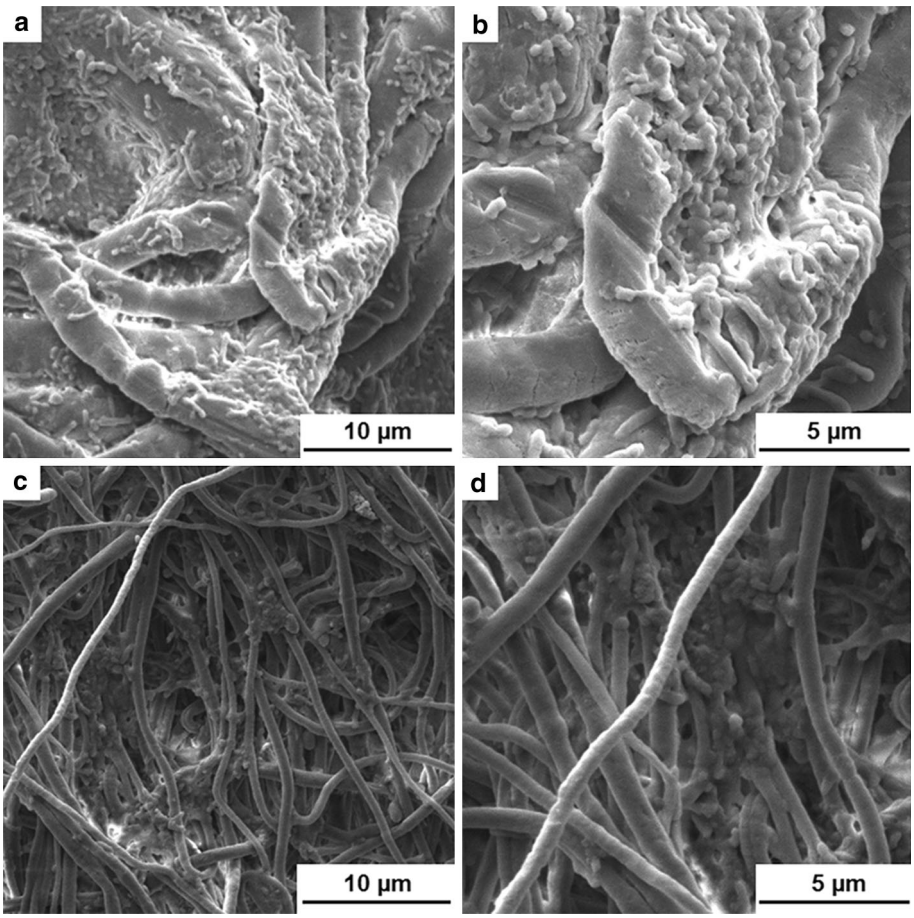


Fig. 5 SEM micrographs of STB5 immobilized **a**, **b** PS and **c**, **d** PSU webs after the reusability tests, showing robust attachment of bacterial biofilms on fibrous surfaces at **a**–**c** ×5000 and **b**–**d** ×10,000 magnification

generated biocomposites were evaluated. It was found that bacterial cells could attach strongly on fibrous surfaces, the biocomposites have the capability to remediate Cr(VI) as effectively as free STB5 cells, they can be reused for several cycles of Cr(VI) removal and they can be stored without losing their Cr(VI) bioremoval capabilities. Similar approaches have been proposed in the literature for remediation of water contaminants, and there are some examples for treatment of water systems by using biointegrated electrospun nanofibrous structures. A novel biocomposite has been produced by Eroglu and colleagues for nitrate bioremoval by immobilizing microalgal cells on electrospun chitosan nanofiber mats (Eroglu et al. 2012). In very recent studies, specific bacterial or algal strains have been immobilized on electrospun nanofibrous webs for ammonium bioremoval (Sarioglu et al. 2013), methylene blue dye biodegradation (San et al. 2014), reactive dye biodegradation (San-Keskin et al. 2015a, b), anionic surfactant biodegradation (Sarioglu et al. 2015) and simultaneous removal of Cr(VI) and a reactive dye (San-Keskin et al. 2015a, b). In the current study, Cr(VI) was selected as the target contaminant, and two different bacteria-immobilized electrospun fibrous webs were prepared to evaluate their Cr(VI) remediation profiles. It was found that Cr(VI) removal performance of STB5 strain decreases at higher concentrations, suggesting that this strain and the biocomposites may be more suitable for bioremediation of freshwater systems with lower amounts of Cr(VI) contamination. By increasing the coverage area of immobilized bacteria in STB5/PS and STB5/PSU webs, or optimizing the bacterial growth conditions, it is likely that higher removal rates for Cr(VI) can be achieved for both biocomposites.

In brief, Cr(VI) removal by STB5/PS and STB5/PSU biocomposites is handy, effective and easily applicable. The results suggest that both biocomposites have the potential to be further developed for use in Cr(VI) remediation from aqueous environments.

Conclusion

In this report, two novel biocomposite materials which are produced by immobilizing a Cr(VI)-removing bacterial strain on electrospun PS and PSU fibrous webs are described. SEM micrographs of STB5/PS and STB5/PSU

web samples have shown robust bacterial adhesion on both fibrous surfaces after incubation time, and no significant differences were observed for the bacterial immobilization even after five cycles of reuse. It was found that the Cr(VI) removal capability of STB5/PS and STB5/PSU biocomposites is based primarily on bacterial activity and is comparable to the Cr(VI) removal performance of free bacterial cells. Considerable amounts of Cr(VI) were removed by both STB5/PS and STB5/PSU biocomposite webs at all tested concentrations, yet the removal performances were started to decrease at higher concentrations, suggesting that the biocomposites can perform best at a defined concentration range. STB5/PS has shown higher removal performances than STB5/PSU in most experiments, implying that higher hydrophobic surfaces of PS webs allowed higher bacterial immobilization for hydrophobic STB5 cells, and thereby higher Cr(VI) removal performances. Both biocomposites were found to be reusable for several cycles and could be stored for short periods of time without exhibiting losses in attached cell numbers or Cr(VI) remediation capabilities, proposing that they may be used repeatedly for Cr(VI) remediation. Free-standing STB5/PS and STB5/PSU biocomposites may be easily utilized for continuous Cr(VI) remediation in freshwater sources by immersing them into the contaminated source.

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