Application of polyaniline for the reduction of toxic Cr(VI) in water

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Abstract

Various oxidation states of polyaniline, as film and powder, were used for reduction of highly toxic Cr(VI) to less toxic Cr(III) ion. The effects of various parameters such as synthesis method, physical and oxidation state of polyaniline, film thickness, solution pH and initial Cr(VI) concentration on the kinetics and efficiency of reduction process were investigated. Results showed that a very broad concentration range of Cr(VI) solutions ($10–10^5$ ppb by emeraldine base and $10–10^{6.5}$ ppb by leucoemeraldine) can be efficiently (>98%) reduced by polyaniline as film or powder. Cr(VI) solutions with concentrations higher than these ranges were caused to the overoxidation and degradation of polymer. Decreasing of solution pH, increased the kinetics and performance of reduction process, but lowered the Cr(VI) concentration ranges caused the overoxidation and degradation of the polymer. Higher reduction efficiencies were obtained for thicker electrochemically synthesized polyaniline films and for thinner chemically prepared polyaniline free standing films. The ability or capacity of various forms of polyaniline in Cr(VI) reduction was evaluated as the milligrams of Cr(VI) reduced by one gram of various forms of polyaniline.
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1. Introduction

Conducting polymers have become one of the most attractive subjects of investigation in last decades. Their unique properties such as electrical conductivity and electrochemical properties (like metals), mechanical strength and ease of processing (like polymers) and possibility of both chemical and electrochemical synthesis, make them useful in wide area of applications. These materials have been used in many applications, including rechargeable batteries [1,2], chemical and electrochemical sensors [3,4], electro-chromic devices [5], corrosion protection [6,7] and switchable membranes [8].

The electrochemical properties and reactions of conducting polymers have been studied extensively [9–11]. In this regard some studies have focused on electrochemical interaction of conducting polymers with toxic metals [12–14]. Results of these studies have lead to the application of conducting polymers in analysis [4,14–17] and abatement [18–20] of some toxic metals from the environment.

One of the most important and very toxic metals studied in this regard is chromium hexavalent [Cr(VI)]. The two more significant oxidation states of chromium are Cr(VI) and Cr(III) [21]. Chromium as Cr(VI) and Cr(III) enters to air, water and soil as a result of natural processes and anthropogenic sources such as chromium plating, leather tanning, wood preserving and making of steel and other alloys, bricks, dyes and pigments [22]. Cr(VI) is extremely mobile in the environment and very toxic, carcinogenic and mutagenic to living organisms, whereas Cr(III) is less toxic and can be easily isolated and precipitated using organic and inorganic reagents [21,23]. Thus, most of the methods for removal or abatement of Cr(VI) from environmental samples are based on the reduction of Cr(VI) to Cr(III) followed by precipitation and removal of Cr(III). Conventional reduction methods are based on the treatment of Cr(VI) with reducing agents such as sulfur dioxide or sodium metabisulfite which aren't entirely satisfactory and are accompanied with secondary wastes and high volume of sludge products [13].

The use of conducting polymers for the reduction of very toxic Cr(VI) to less toxic Cr(III) has been reported by Rajeshwar and co-workers first time in 1993 [24]. They have reported the complete reduction (100% efficiency) of Cr(VI) by electrosynthesized polypyrrole films. The advantages of conducting

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polymers for Cr(VI) reduction with respect to usual reducing agents, is the reversibility of reduction process and possibility of recycling of conducting polymers for further treatments. Rajeshwar and co-workers have also reported the catalytic reduction of Cr(VI) by polypyrrole and its composites with carbon black [25–27]. They showed that the content of carbon black in polypyrrole-carbon black composite affects on the reduction process so that the increasing of carbon black content of the composite, caused to an increase in the reduction process performance.

More recently the use of polyaniline films for the reduction of toxic Cr(VI) species in solution has been reported [28,29]. Breslin and co-worker [28] have studied the mechanism and kinetics of Cr(VI) reduction by various oxidation states of electrochemically synthesized polyaniline films. They have also reported the effect of polyaniline film thickness on the efficiency of reduction process.

In all previous works, conducting polymer films have been used for the reduction of Cr(VI) or other toxic metals. However polyaniline can be prepared chemically or electrochemically in various forms such as powder, free standing film or film on electrodes. Also polyaniline, as a reducing agent, have different oxidation states of leucoemeraldine and emeraldine. The aim of this work is to study the efficiency and kinetics of Cr(VI) reduction by various forms of polyaniline. The effect of synthesis method, film or powder form, oxidation state and some other parameters such as polymer film thickness, initial Cr(VI) concentration and solution pH, on the kinetics and performance of Cr(VI) reduction was also studied.

2. Experimental

2.1. Reagents and materials

Hydrochloric acid, sulfuric acid, potassium dichromate, ammonium persulfate, ammonia, acetone and aniline were all purchased from Merck chemicals (Germany) and were used as received without any further purification, except aniline which was distilled under vacuum prior to use.

2.2. Instrumentation

A galvanostat/potentiostat WENKING TG 97 from Bank (Germany) and a pH meter 654 from Metrohm Co. (CH 9101-Herisau, Switzerland) were used for the electrosynthesis of polyaniline and its reduction under potentiostatic condition. A three-electrode electrochemical cell system consisted of a gold coated electrode as working electrode, a platinum gauze as auxiliary electrode and an Ag/AgCl as reference electrode was used for electropolymerization and electrochemical experiments. A micrometer SM 1201 Teclock Corporation (Japan) was used to measure the thicknesses of free standing polyaniline films.

2.3. Polyaniline synthesis

Polyaniline was synthesized both chemically and electrochemically. Chemical synthesis of polyaniline was performed in 1 M HCl solution using $(NH_4)_2S_2O_8$ as oxidant/initiator. The synthesized emeraldine salt form of PANI was dedoped in 1 M ammonia solution for 6 h. The emeraldine base was washed with water and acetone followed by drying in vacuum for 12 h at 60 °C.

For electrochemical synthesis of polyaniline a constant current density of 1 mA/cm^2 was applied to a gold electrode in a solution containing 1 M aniline and 2 M HCl. The synthesized emeraldine salt was washed with water and reduced to leucoemeraldine salt in a potentiostatic route by the application of −0.1 V versus Ag/AgCl in 0.1 M H$_2$SO$_4$ solution.

2.4. Reduction of Cr(VI) by polyaniline

Polyaniline was used for reduction of Cr(VI) in solution. The chemically and electrochemically synthesized polyaniline in powder or film forms were exposed to the solutions of Cr(VI) in different concentrations. The Cr(VI) solutions were prepared in different concentrations by dissolution of potassium dichromate in distilled water (pH ∼ 7) and in acidic media of H$_2$SO$_4$ solution (pH ∼ 1 or 3). The Cr(VI) solutions were stirred (600 rpm) during the exposure to various forms of polyaniline. The concentration of Cr(VI) in solution was measured after different exposure times. A spectrophotometric technique was used for determination of Cr(VI) concentration in solution. The UV–vis absorption spectra of Cr(VI) solutions were recorded at regular intervals between 200 and 800 nm using a WPA 5200 (England) UV-Vis spectrophotometer. For Cr(VI) solutions with the concentrations of higher than ∼10^4 ppb the peak intensity at ∼355 nm was used for evaluation of Cr(VI) concentration, but in the case of Cr(VI) solutions with the concentrations of lower than ∼10^4 ppb the diphenilcarbazide method was used at a wave length of 540 nm [30].

The efficiency of reduction reaction was calculated according to the Eq. (1):

$$R = \frac{100(C_0 - C_t)}{C_0} \tag{1}$$

where C_0 is the initial concentration of Cr(VI) in solution and C_t is the concentration of Cr(VI) after a certain time of exposure to polyaniline film or powder.

3. Results and discussion

3.1. Reduction of Cr(VI) by chemically synthesized polyaniline

Polyaniline powder as emeraldine salt (ES) form was obtained via chemical synthesis route. The ES was treated with ammonia solution (1 M) for 6 h to obtain the reductant emeraldine base (EB) form of polyaniline. Different amounts of the chemically synthesized polyaniline powder, in the emeraldine base form, were added to 10 ml of Cr(VI) solutions with different concentrations. The exposure was performed in different times followed by filtration and separation of polyaniline particles.

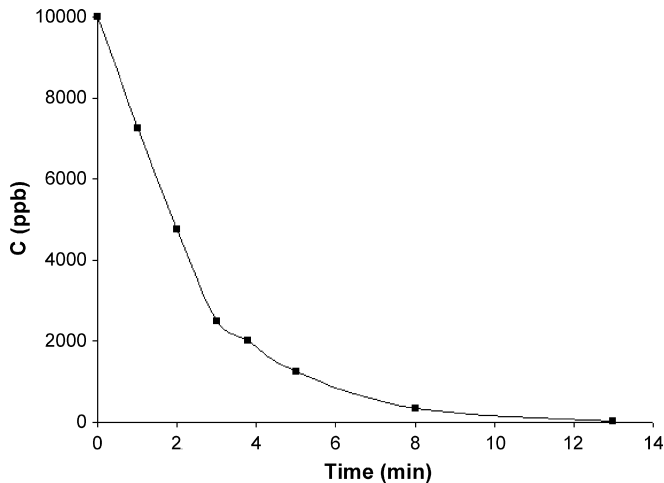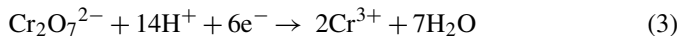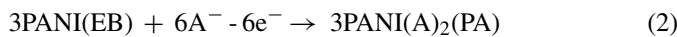The emeraldine base form of polyaniline can be oxidized to pernigraniline (PA) which is accompanied by reduction of

Fig. 1. Changes in the concentration of Cr(VI) solution (pH = 7), with 10^4 ppb initial concentration, during the exposure to 0.01 g EB powder.

Fig. 2. Total reduction efficiency of Cr(VI) in a 10^5 ppb Cr(VI) solution (pH = 7) by the application of various amounts of EB powder, after 30 min of exposure.

Cr(VI) in solution:

$$3PANI(EB) + 6A^- - 6e^- \rightarrow 3PANI(A)_2(PA) \qquad (2)$$

$$Cr_2O_7{}^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad (3)$$

where PANI represents one tetramer and A^- is the anion present in solution (OH^- in distilled water and $HSO_4{}^-$ in acidic H_2SO_4 solution). Using the spectrophotometric technique, the concentration of Cr(VI) in solution was determined before and after different times of exposure to the polyaniline (EB) powder. Fig. 1 shows the changes in the concentration of Cr(VI) with the initial concentration of 10^4 ppb during exposure to 0.01 g of emeraldine base(EB) powder.

It is obvious that the amount of polyaniline powder added to the Cr(VI) solution, is effective on the total performance of Cr(VI) reduction. On the other hand the amount of polyaniline needed to efficient reduction of Cr(VI) depends on the concentration of Cr(VI) in solution. To obtain the optimum amount of polyaniline needed to effectively reduce Cr(VI) in the concentration range of $10–10^5$ ppb (from an acceptable concentration value in drinking water to a high concentrated medium which may be found in a polluted wastewater), various amounts (0.005 to 0.05 g) of emeraldine base powder were added to a 10 ml of Cr(VI) solution with a high initial concentration of 10^5 ppb, and the total reduction efficiency against the added amount of EB powder was evaluated after 30 min of exposure (Fig. 2). It was found that the application of 0.03 g EB is enough for reduction of Cr(VI) with an efficiency of higher than 99.9%. Therefore it was concluded that 0.03 g is an enough optimum weight of EB for the reduction of 10 ml of Cr(VI) solutions with the maximum concentration of 10^5 ppb. Thus, application of this amount of EB powder for lower concentrations of Cr(VI) solutions, caused to the complete reduction of Cr(VI) in solution.

3.2. Optimum time of reduction

Further experiments were carried out to evaluate the optimum time needed for high efficiency reduction of Cr(VI) solutions with different initial concentrations. The Cr(VI) solutions with
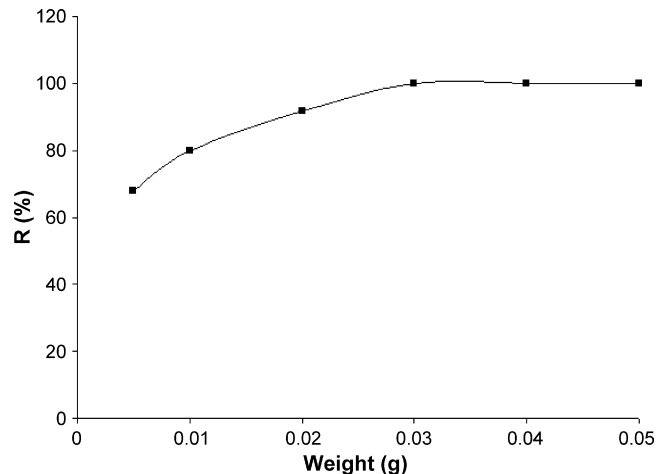
different initial concentrations, in the range $10–10^5$ ppb, were exposed to the same amount (0.03 g) of EB powder. The concentration of Cr(VI) after exposure to EB powder versus its initial concentration (C_t/C_0) were plotted against time (Fig. 3). According to the results, it was found that the reduction efficiency increases by increasing the treatment time and an exposure time of ~16 min is enough to high efficiency (>99.9%) reduction of Cr(VI) solutions with different initial concentrations.

3.3. The effect of initial concentration of Cr(VI)

The concentration of Cr(VI) in solution determines not only the toxicity of the solution but also the oxidizing power of the solution. It seems important to know the ability or capacity of various forms of polyaniline to reduce highly concentrated Cr(VI) solutions. Further experiments were carried out to evaluate the ability of chemically synthesized EB powder for the reduction of Cr(VI) solutions with various initial concentrations. For this, a high value (2 g) of EB powder, which was theoretically enough to reduce very concentrated Cr(VI) solutions up
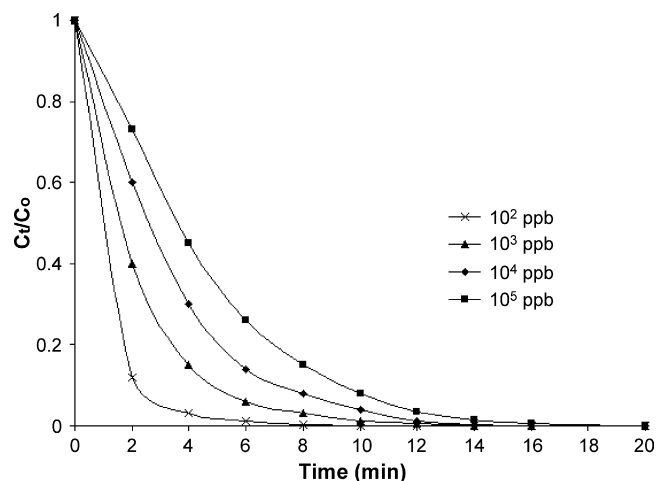

Fig. 3. Normalized concentration depletion of Cr(VI) solution (pH = 7) with different initial concentrations, during exposure to 0.03 g EB powder.
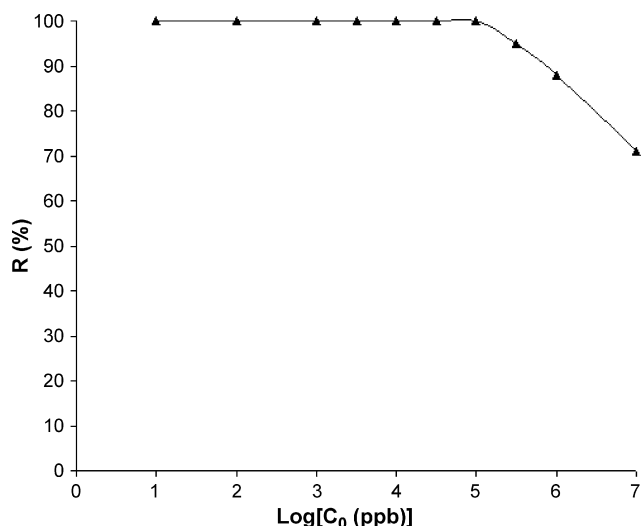
Fig. 4. Reduction efficiency of Cr(VI) solution against the initial concentration of Cr(VI) in solution (pH = 7), after 16 min of exposure to 2 g EB powder.

to 10^7 ppb, was used for the reduction of various concentrations ($10–10^7$ ppb) of Cr(VI) solutions. Fig. 4 shows the reduction efficiency of Cr(VI) in solution, with different initial concentrations, using the same amount (2 g) of EB powder in the same reduction time (16 min). Results showed that EB powder can be used to reduce 10 ml of Cr(VI) solutions in the concentration range of $10–10^5$ ppb with reduction efficiencies of higher than 99.9%. However, in Cr(VI) solutions with the concentrations higher than 10^5 ppb, the reduction efficiency decreases by increasing of the Cr(VI) concentration. This is due to the high oxidative environment of concentrated Cr(VI) solutions which causes to the overoxidation and degradation of polyaniline [3]. Therefore the EB powder can be used for the reduction of toxic Cr(VI) in neutrally pH solutions (pH $\sim$ 7) with the initial concentrations in the range $10–10^5$ ppb.

3.4. Effect of solution pH

The half reduction reaction of Cr(VI) is pH dependent (Eq. (3)). The reaction progress and kinetics increases by decreasing of solution pH. That is to say, the oxidizing power of Cr(VI) component increases by pH decreasing. According to the results of previous section, the oxidizing power of Cr(VI) affects on the polyaniline stability in solution. Therefore effect of pH on the process of Cr(VI) reduction by polyaniline powder was investigated. The Cr(VI) solutions with different pH values (pH $\sim$ 1, 3, 7) were prepared. Because of the increasing of reduction process efficiency in acidic environments, only the acidic pH values were studied. The pH of Cr(VI) solutions was adjusted by addition of sulfuric acid solution. Fig. 5 typically shows the changes in the concentration of Cr(VI) in solutions, with the same initial concentration of Cr(VI) (10^3 ppb) but with different pH values, during exposure to 0.03 g EB powder. It can be seen that the reaction kinetics increases by increasing the acidity of Cr(VI) solutions. However the reduction efficiency after $\sim$16 min of exposure is almost similar for all three solutions with different pH values. Also the reduction efficiency of Cr(VI) solutions
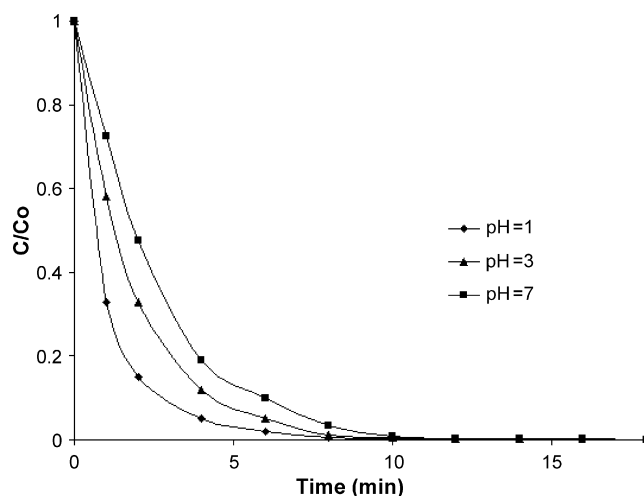

Fig. 5. Normalized concentration depletion of 10^3 ppb Cr(VI) solution with different pH values, during exposure to 0.03 g EB powder.

with different initial concentrations of Cr(VI) and different pH values was obtained after $\sim$16 min of exposure to EB powder (Fig. 6). It was found that by increasing the solution acidity, the overoxidation and degradation of polyaniline, occurs in lower concentrations of Cr(VI) solutions. This is due to the increasing of oxidizing power of Cr(VI) component in acidic environments. Therefore it can be concluded that the reduction kinetics is higher in acidic solutions, but the upper concentration range of Cr(VI) which can be reduced by EB powder is limited by decreasing of the pH.

3.5. Effect of exposure time

In other series of experiments, the free standing polyaniline film was used for the reduction of Cr(VI) in solution. Solution casting method was used for the preparation of polyaniline free standing films. Chemically synthesized EB powder was dissolved in *N*-methyl pyrrolidone and casted on a glass plate. The
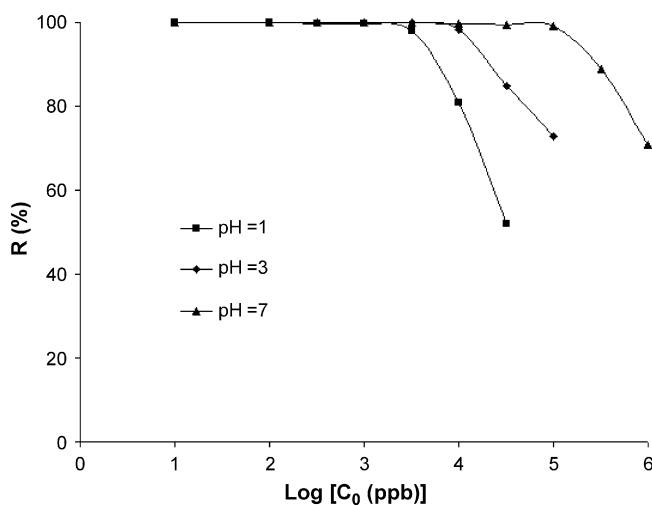

Fig. 6. Reduction efficiency of Cr(VI) solutions, with different pH, after 16 min of exposure to 0.03 g EB powder, against the initial concentration of Cr(VI) in solution.
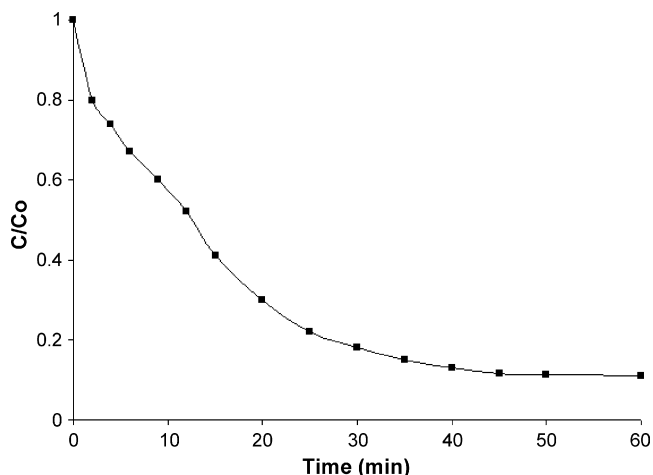
Fig. 7. Normalized concentration depletion of 10^3 ppb Cr(VI) solution (pH = 7) against time, during exposure to chemically synthesized EB free standing film with 0.03 g weight and 150 μm thicknesses.

free standing film was released from the glass surface after solvent evaporation. The film was immersed in Cr(VI) solutions under vigorous stirring conditions.

Fig. 7, typically shows the normalized concentration depletion of a Cr(VI) solution with 10^3 ppb initial concentration against time during exposure to an EB free standing film with the 0.03 g total weight and 150 μm thicknesses. To make a comparison between EB powder and EB film in Cr(VI) reduction, the same weight (0.03 g) of films were applied in Cr(VI) reduction. It is clear that the surface area of the films with the same weight can be varied by the variation in the film thicknesses because, to obtain a thinner films from the same amount of polymer, polymer solution should be casted in a larger surface glass area.

Fig. 8 shows the reduction efficiency of Cr(VI) by the same weight (0.03 g) of EB free standing films, but with different film thicknesses. It was found that, the reduction efficiency decreases by increasing of the polymer film thicknesses. This is due to the increasing of surface area of the film by decreasing of its thicknesses. However non-linear increasing of the reduction effi-
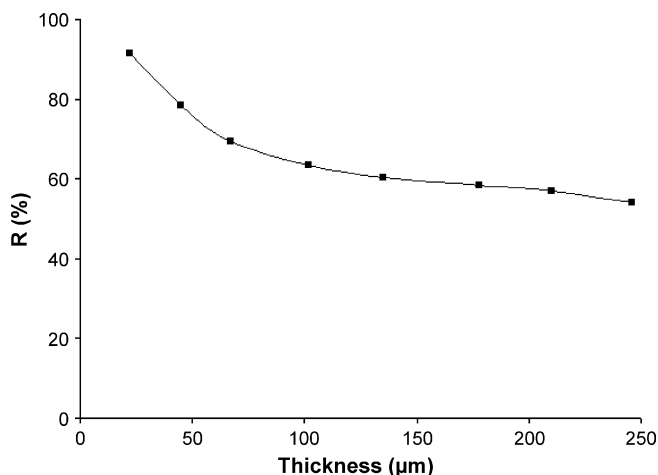
ciency (the slope of the graph in Fig. 8 varies with thickness variation), may be due to the increasing of diffusion and diffusion rate of the Cr(VI) into the polymer film, by decreasing of the film thicknesses.

According to the results, even in very thinner polymer films, the total reduction efficiency of the EB film was lower than the reduction efficiency of EB powder with the same weight. Further experiments showed that similar to EB powder, the reduction efficiency of Cr(VI) by EB free standing film increases by increasing of solution acidity and falls down due to the degradation of polymer film in more acidic or concentrated Cr(VI) solutions (Fig. 6).

3.6. Reduction of Cr(VI) by electrochemically synthesized polyaniline film

Electrochemically synthesized polyaniline film was also applied for the reduction of Cr(VI) solutions. A thin layer of polyaniline was prepared on a gold coated electrode by the application of a constant current density of 1 mA/cm^2 in a solution containing aniline (1 M) and HCl (2 M). A green layer of polyaniline (emeraldine salt form (ES)) was formed on gold electrode. In order to have polymer films with different thicknesses, the electropolymerization was proceed in different times. To obtain the EB form of polyaniline on gold electrode, the electrochemically synthesized ES was treated with ammonia solution (1 M) for 6 h. To have the fully reduced leuocoemeraldine (LE) form of polyaniline on gold electrode, the electrochemically synthesized ES film was reduced in −0.1 V constant potential versus Ag/AgCl reference electrode in H$_2$SO$_4$ (0.1 M) solution for 20 min.

3.6.1. Effect of oxidation state of polyaniline on Cr(VI) reduction

Both the emeraldine base and leuocoemeraldine forms of electrochemically synthesized polyaniline films were applied for the reduction of Cr(VI) solutions. In each case, the film was immersed in Cr(VI) solution with different concentrations and the reduction efficiency of Cr(VI) was evaluated by spectrophotometric analysis of Cr(VI) concentration after different exposure times. Fig. 9 shows the changes in the concentration of a Cr(VI) solution with the initial concentration of 10^4 ppb, during the exposure to EB and LE forms of electrochemically synthesized polyaniline films (film thicknesses: ∼150 μm and film weights: 0.03 g). It is obvious that LE is a stronger reducing agent in comparison with EB, because it has more amine nitrogens and can loss four electrons per each tetramer. Thus it has higher reducing capacity than EB form. As shown in Fig. 9, a contact time of about 30 min is enough for the reduction of different concentrations of Cr(VI) by the reduction efficiencies of higher than 98%.

3.6.2. Effect of polyaniline film thickness on the Cr(VI) reduction

To investigate the effect of electrochemically synthesized polyaniline film thickness on the Cr(VI) reduction efficiency, the EB and LE films with different thicknesses were prepared.
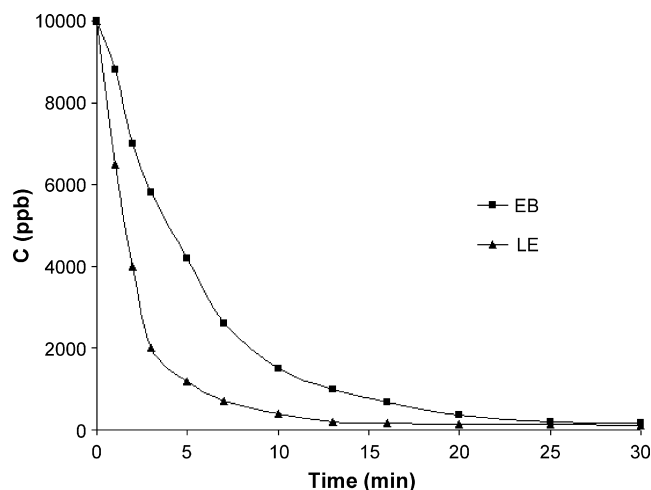

Fig. 8. Total reduction efficiency of a 10^3 ppb Cr(VI) solution (pH = 7) by 0.03 g chemically prepared EB free standing film as a function of film thicknesses.

Fig. 9. Concentration changes of 10^4 ppb Cr(VI) solution (pH = 7) against time, during exposure to electrochemically synthesized LE and EB films with 0.03 g weight and ~150 μm thicknesses.

Fig. 10 shows the reduction efficiency of a Cr(VI) solution (10^3 ppb) after a constant exposure times to EB and LE films with different thicknesses. In opposite to the chemically synthesized free standing films, increasing of the thicknesses of the electrochemically synthesized polyaniline films causes to the increasing of the reduction efficiency. This behavior together with the higher reduction efficiencies of electrochemically synthesized films may be due to the higher porosity structure of electrochemically synthesized films against to the chemically synthesized free standing films.

3.6.3. Effect of solution pH

Further experiments with electrochemically synthesized polyaniline films, showed that the effect of solution pH and initial Cr(VI) concentration on the reduction efficiency is similar to chemically synthesized free standing films (Fig. 11). However due to the higher reduction capacity of LE film, it can be used for reduction of more concentrated Cr(VI) solutions ($10^{6.5}$ ppb) without overoxidation and degradation.
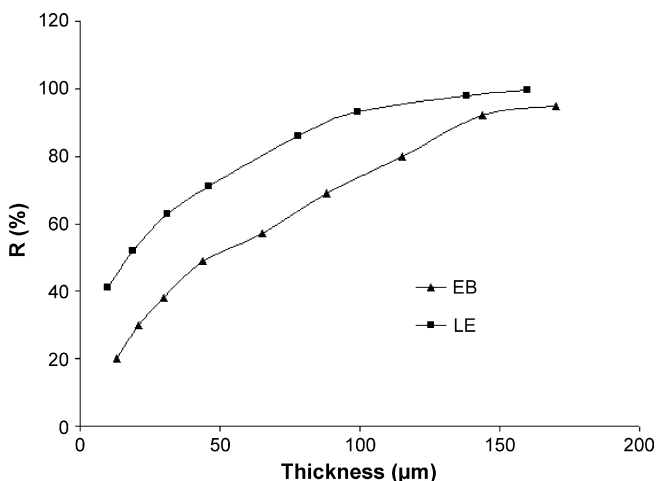

Fig. 10. Total reduction efficiency of 10^3 ppb Cr(VI) solution (pH = 7) by electrochemically prepared LE and EB films as a function of film thicknesses.
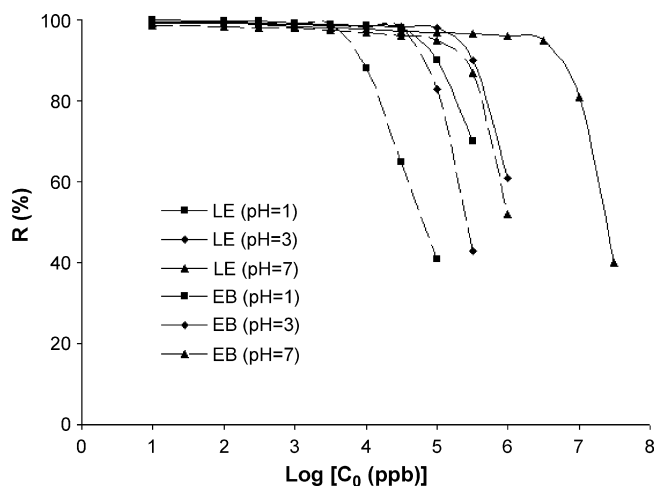

Fig. 11. Reduction efficiency of Cr(VI) solution in different pH values, after 30 min of exposure to electrochemically synthesized leucoemeraldine(LE) and emeraldine base (EB) films, against the initial concentration of Cr(VI) in solution.

Table 1
Special reduction performance (SPR) for Cr(VI) reduction by various forms of polyaniline, after 30 min of exposure, in neutral pH

State	S.R.P. (mg/g)
PANI powder (EB)	74
PANI film (free standing) (EB)	50
PANI film (free standing) (LE)	80
PANI film (on electrode) (EB)	61
PANI film (on electrode) (LE)	96

3.7. Special reduction performance

Finally, for a total comparison between all forms of polyaniline (discussed above) in Cr(VI) reduction performance, the amount (milligrams) of Cr(VI) component which can be reduced by one gram of each form of polyaniline in neutral solution (pH ∼ 7) was evaluated as the special reduction performance. In the other word the special reduction performance of each form of polyaniline represents the performance of its mass unit in reduction of Cr(VI). In this experiment all forms of polyaniline were exposed to the same concentration of Cr(VI) solutions (10^5 ppb) in a similar exposure time (30 min). The change in the concentration of Cr(VI) in solution after exposure time was converted to milligrams of Cr(VI) reduced by different forms of polyaniline. Using the mass of the various forms of polyaniline used in this experiment, the special reduction performance was calculated (Table 1). It should be noted that, using the quartz crystal microbalance technique, the weights of electrochemically synthesized polyaniline films were obtained and used in special reduction performance calculation [3].

4. Conclusion

Chemically and electrochemically synthesized polyaniline as powder and film forms can be used to reduce very toxic Cr(VI) to less toxic Cr(III) in aqueous solutions. With increasing the

thickness of the polyaniline films prepared electrochemically in contrast to polymer films synthesized chemically, the reduction performance of the polymer for Cr(VI) is increased. High concentrations of Cr(VI) causes to the overoxidation and degradation of all forms of polyaniline. Increasing the acidity of Cr(VI) solutions was increased the kinetics and efficiency of reduction but overoxidation and degradation of polyaniline in acidic conditions occurs in lower concentrations of Cr(VI).

Acknowledgments

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