



Stability of UV-visible spectrophotometric measurements for investigating the adsorption of hexavalent chromium from wastewater

Maher Al-Jabari*, Hassan Sawalha, Bayan Al-Qasrawi, Malak Al-Osily, Shatha Banat

Environmental Technology Engineering Group, Mechanical Engineering Department, Palestine Polytechnic University, P.O. Box: 198, Wadi Al-Haria, Hebron, Palestinian Authority, emails: mjabari@ppu.edu (M. Al-Jabari), hsawalha@ppu.edu (H. Sawalha), bayan.qtamimi@gmail.com (B. Al-Qasrawi), malak.al.osily@gmail.com (M. Al-Osily), chada_banat@hotmail.com (S. Banat)

Received 11 April 2022; Accepted 1 July 2022

ABSTRACT

Hexavalent chromium Cr(VI) is a carcinogenic and mutagenic heavy metal. It can be encountered in various industrial wastewater, the characterization of which and the evaluation of its removal efficiency require a successful quantification technique. There is no sufficient work in the literature investigating the time-stability of UV-vis spectra of Cr(VI) solutions. This paper fills a knowledge gap in Cr(VI) solution/color stability and the applicability of UV-spectrophotometry in Cr(VI) adsorption studies. The presented experimental results indicate that the absorbance of Cr(VI) solution at the previously reported maximum wavelength of 371 nm, is not repeatable. The addition of 1,5-diphenylcarbazide improves the UV-vis spectra and enhances its stability for spectrophotometric analysis within about 1 h. After that period, the stability decreases with time. The instability of these spectrophotometric measurements at longer times (i.e., after 1 h) was not reported in the previous studies or in the ISO standard method for determining the Cr(VI). This paper also applies this technique for monitoring and evaluating the adsorption treatment of Cr(VI)-contaminated wastewater (e.g., from electroplating) by solid waste micro-particles from stone cutting industry. The limestone particles are good adsorbents for the treatment of wastewaters contaminated with Cr(VI). A percentage removal of about 40% can be achieved for adsorbent dosage of 1 g (particles)/100 ml (solution).

Keywords: UV-visible spectrophotometry; Hexavalent chromium; Wavelength; Adsorption

1. Introduction

Wastewater contaminated with hexavalent chromium, Cr(VI), is characterized as a hazardous waste. It can be released from electroplating, in which, ionic metal is coated using a chemical solution of heavy metals such as Cr(VI) and zinc. Cr(VI) contaminated wastewater can also be released from textile industry, wood preservation, dyes and pigments, and other aluminum surface treatment.

Wastewater contaminated with Cr(VI) has major impacts on environment and public health. According to the World Health Organization (WHO), the designated guideline value for chromium is set at 50 µg/L for in drinking water [1,2], while the allowable limit for Cr(VI) in water as given by the US environmental protection agency is 0.1 mg/L [3,4]. Low-level exposure of human to Cr(VI) can cause irritation to the skin and ulceration [5,6]. Whereas,

* Corresponding author.

Presented at the 1st Palestinian-Dutch Conference on Water, Sanitation and Hygiene (WASH), and Climate Smart Agriculture (CSA), 5–6 September 2022, Nablus, Palestinian Authority

1944-3994/1944-3986 © 2022 The Author(s). Published by Desalination Publications.

This is an Open Access article. Non-commercial re-use, distribution, and reproduction in any medium, provided the original work is properly attributed, cited, and is not altered, transformed, or built upon in any way, is permitted. The moral rights of the named author(s) have been asserted.

long-term exposure leads to kidney and liver damage, and severely harm circulatory and nerve tissue [6]. When wastewater is discharged to sea, the Cr(VI) accumulates in fish tissues and consequently transfers to the human through food [7–9]. Consequently, treating wastewater contaminated with Cr(VI) is of high priority for both environment and public health. Various treatment technologies have been used for the removal of Cr(VI) from wastewater. These include adsorption [10–15], membrane technology [16,17], ion exchange [18,19], etc. Various types of adsorbents have been used for the removal of the two states of chromium(III and VI). These include kaolin clay [19], rice husk, silica powder [20], magnetic (FeO_4) nanoparticles [21], activated carbon and carbon nanotubes [20], bio-char derived from municipal sludge [22], corn stalk [23], magnetic natural zeolite polymer [24] and sawdust [25]. In other previous work, the focus was on the adsorption of Cr(III) on other types of adsorbents including mineral particles such as marl and soil particles [26,27] and limestone particles [28]. Additionally, the characteristics of Zn contaminated wastewater from galvanization industry, and the technical feasibility of Zn adsorption on magnetic nano-adsorbent has been also investigated [29].

Several techniques have been reported in the literature for measuring the hexavalent chromium in water solutions including atomic absorption spectrometry, flame atomic absorption spectrometry and colorimetric method. The colorimetric methods can be used for measuring chromium concentrations in water in the range of 100–1,000 $\mu\text{g/L}$. The spectrophotometric techniques suffer from color instability of the Cr(VI) solution with time due to the variations in Cr(VI) complex structure, which greatly affects the accuracy of the measurements. To improve the stability of the Cr(VI) solution, stabilizing reagents such as 1,5-diphenylcarbazide, are commonly added [30]. Most of the previous studies investigated the stability of the system within a short time scale (i.e., up to 10 min) after addition of the stabilizing reagents. However, up to the knowledge of the authors, the instability of the system after longer time periods has not been discussed in the literature. The main goal of the present study is to investigate the applicability of using the UV-spectrophotometric analysis for investigating the technical feasibility of adsorbing Cr(VI) from wastewater on stone cutting powders. Within this context, the stability of the Cr(VI) solution with and without the addition of a stabilizing reagent (1,5-diphenylcarbazide) is studied as a function of time using UV-visible spectrophotometer.

2. Experimental work and analysis

2.1. Materials

Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) was used as a source for Cr(VI). 1,5-diphenylcarbazide solution in acetone was used as a stabilizing reagent. NaOH and HCl were used for adjusting the pH of the system. All the primary chemicals used in this study were of analytical grade. For adsorption experiments, stone cutting limestone particles were collected from local stone cutting plant (Hebron, Palestine) and used as adsorbent.

2.2. Methods

2.2.1. Preparation of stock solutions

A stock solution of Cr(VI) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in NaOH and distilled water. Then, various dilutions were prepared accordingly. The 1,5-diphenylcarbazide solution was prepared by dissolving 250 mg of 1,5-diphenylcarbazide (1,5-diphenylcarbohydrazide) in 50 mL acetone. Then, 2 ml of this solution was added, when required, to the Cr(VI) solution as a stabilizing reagent.

2.2.2. Spectrophotometric analysis

Several Cr(VI) solutions were prepared by diluting the stock solution to various concentrations. The absorbance of the solutions was measured using UV-visible spectrophotometer (BOECO, Hamburg, Germany). A calibration curve of Cr(VI) vs absorbance was constructed accordingly. The maximum wavelengths for the two types of solutions (with and without a stabilizing reagent) were obtained.

2.2.3. Batch adsorption tests

A known amount of adsorbent (limestone particles) was added to 100 mL of Cr(VI)-solution in volumetric flask. The suspension was then stirred for the required time period using a rotary shaker (EL.MI Intelli-Mixer RM 2L, Latvia). The mixture was then filtered through filter paper and the concentration of Cr(VI) in the solution was determined through measuring the absorbance of the sample using UV-Visible spectrophotometer. All experiments were conducted at ambient room temperature ($\sim 20^\circ\text{C}$ – 25°C).

3. Results and discussion

The results are divided into two main sections. In the first section, the instability of Cr(VI) solutions and the validity of UV-spectrophotometric analysis is discussed. The second section deals with the Cr(VI) wastewater treatment through batch adsorption onto limestone particles.

3.1. Instability of Cr(VI) solution

The UV-visible spectra of the Cr(VI) stock solutions without adding a stabilizing reagent for solutions with different Cr(VI) concentrations and at different time intervals after solution preparation are shown in Fig. 1. It can be seen that the maximum wavelength of the various solutions occurs at nearly 371 nm, which is in agreement with reported values in the literature [31]. However, the absorbance of Cr(VI) solution varied with concentration and time. A clear shift in the curves towards lower absorbance could be observed with decreasing Cr(VI) concentration (Fig. 1a). Additionally, the absorbance was observed to change with time (Fig. 1b). Changes in the maximum wavelengths and the absorbance (for the same solution) could be attributed to the variations in Cr(VI) complex structure [31]. Such a time instability creates complications in the direct use of UV-spectrophotometry for Cr(VI) analysis. The observed shifts in the absorbance can be wrongly interpreted in the adsorption results as being

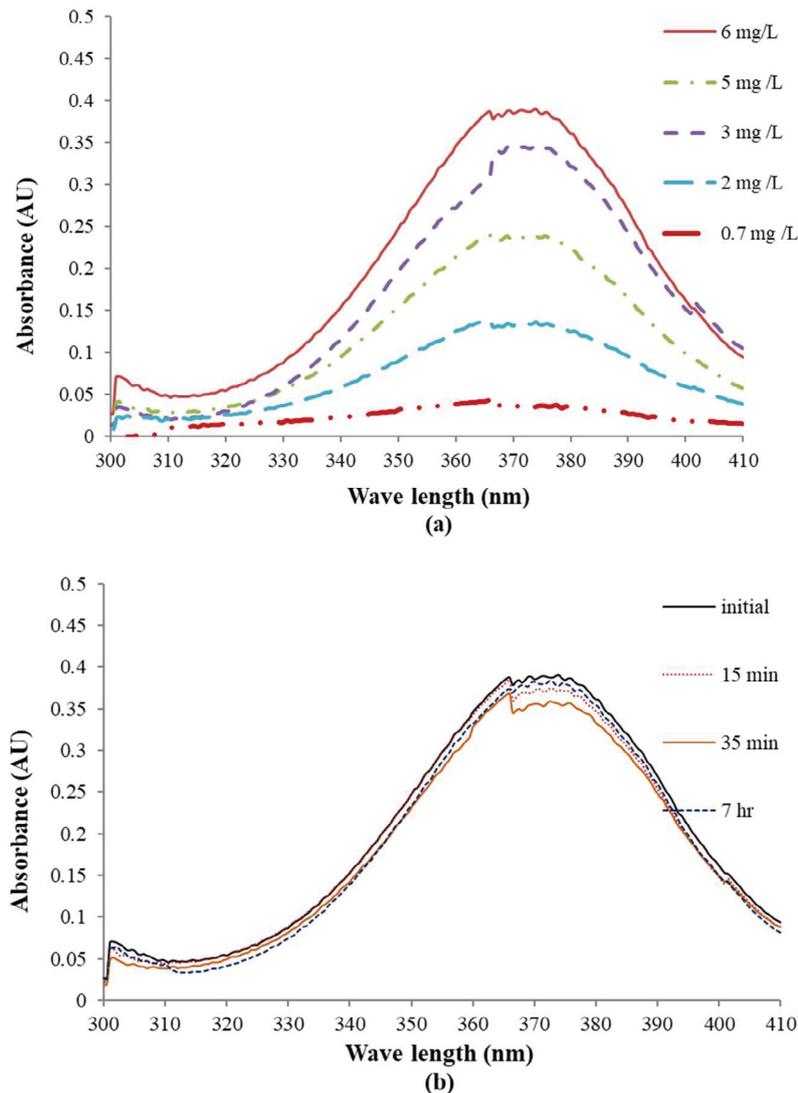


Fig. 1. The measured spectra for: (a) various dilutions of Cr(VI) solution (6, 5, 3, 2, and 0.7 mg/L) and (b) for a solution of 6 mg/L at different times intervals from the time of preparation. All measurements were performed at room temperature, pH = 12 and without adding a reagent.

due to adsorption while it can be resulting from time instability of the UV-spectrophotometric analysis. These observations (e.g., Fig. 1b) raise inquiries on the accuracy of the previous works used such an approach for investigating adsorption on various adsorbent particles without paying attention to the measurement time and change in concentration. The impracticality of measuring Cr(VI) concentration at 371 nm was not mentioned in any of the previous studies, up to the knowledge of the authors.

For further assessment of the applicability of UV-spectrophotometry for Cr(VI) analysis, the maximum wavelength of Cr(VI) solution without reagent was measured with time as shown in Fig. 2. Noticeable variations in the maximum wavelength with time can be observed clearly in Fig. 2; the stability in these measurements could not be maintained for plain solutions of Cr(VI). On the other hand, Fig. 3 shows the maximum wavelength of Cr(VI) solution

after adding the stabilizing reagent (1,5-diphenylcarbazide) with time. When the reagent 1,5-diphenylcarbazide was added to Cr(VI) solutions, the maximum wavelength of the solution remains fairly constant with time at 540 nm (Fig. 3). These observations are in agreement with the reported maximum values [23,24,32].

Furthermore, the stability of the absorbance of the Cr(VI) solution with time (with and without reagent) is shown in Fig. 4. Without a stabilizing reagent, the absorbance measurements were clearly instable with time over the whole period of measurements. On the other hand, with addition of the stabilizing reagent, three time periods of measurements can be identified. In the first 10 min, the absorbance changes considerably with time and the measurements were instable. In the second period (10–60 min), stability in the measurements was achieved as the absorbance remained almost constant with time. In the third

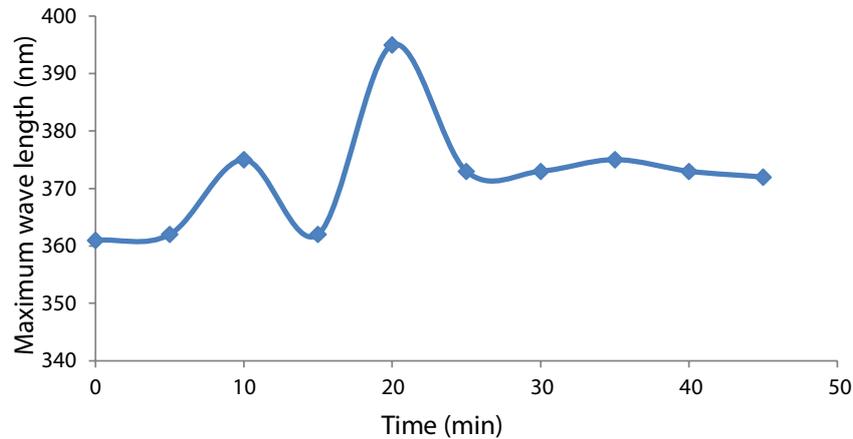


Fig. 2. The measured maximum wave length for Cr(VI) solution with time without adding a reagent for a solution concentration of 6 mg/L at room temperature and pH = 12..

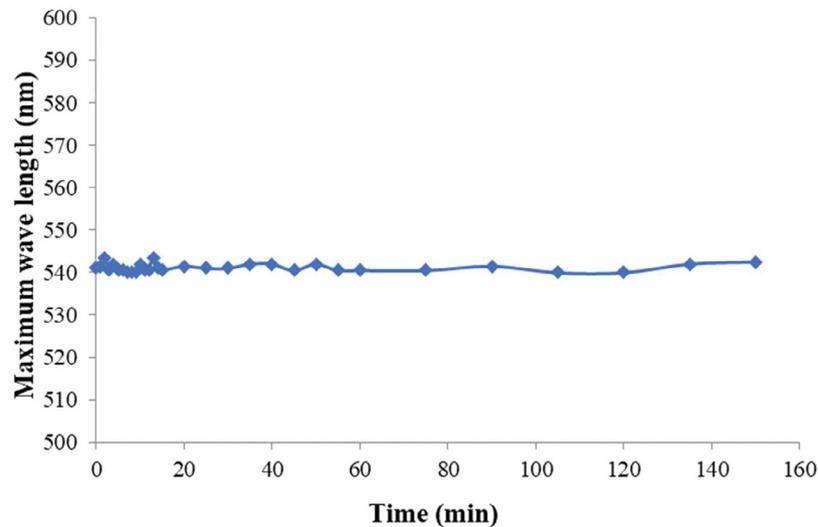


Fig. 3. The measured maximum wave length for Cr(VI) solution with time with the addition of 1,5-diphenylcarbazide reagent for a solution concentration of 6 mg/L at room temperature and pH = 12.

period (after 1 h of solution preparation), the absorbance increased with time and the system became instable again (Fig. 4).

In the previous studies, the absorbance of Cr(VI) solution was usually measured after 10 min of preparation [30]. This seems to be based on the ISO standard method (ISO 17075:2007(E)) for determination of Cr(VI) content, which stated that the solution should stand for 15 ± 5 min before measuring the absorbance at 540 nm. Obviously, the reported method is valid, since a repeatable constant value of absorbance (for the same solution) can be obtained when measurements are made after 10 min of preparations. However, neither of the previous studies, nor the standard method tested the stability of these measurements after longer times (i.e., 1 h) and none reported on the behavior of the subsequent instability. This can create a technical problem particularly if the absorbance needs to be measured after 1 h of preparation as in the case of adsorption experiments.

The instability of the Cr(VI) solution can interfere with the actual results (i.e., percentage removal of pollutant from wastewater) then wrong conclusions may be drawn. Thus, it is essential to limit the time period for UV spectrophotometric analysis of Cr(VI) solutions (using 1,5-diphenylcarbazide) between 10–60 min after adding the reagent. For the case without using a reagent, no stability could be obtained (Fig. 4). This confirms the importance of analysis of Cr(VI) solutions using 1,5-diphenylcarbazide as a stabilizing reagent.

3.2. Effect of pH on the stability of Cr(VI) solutions

In most of the adsorption studies, pH is an important operating parameter. In some cases, when the adsorbents are alkaline as in the case of stone cutting particles, the pH of the wastewater changes after the addition of the particles due to the partial solubility of lime from the particles [28]. Hence, it is essential to investigate the stability of UV-vis

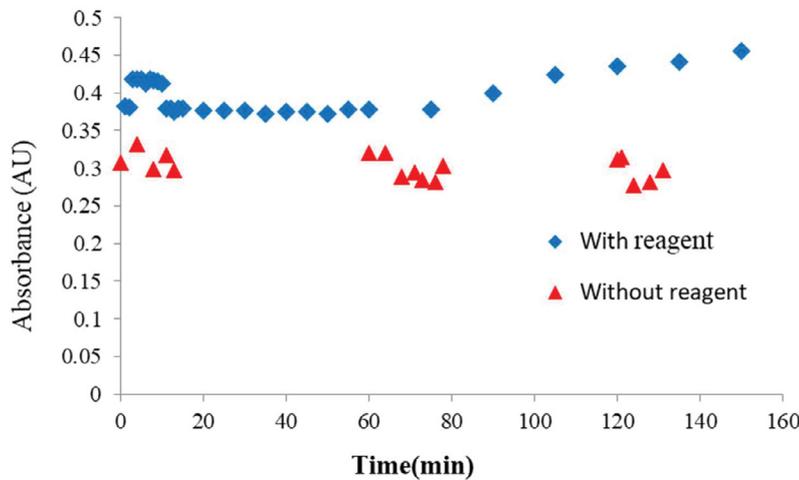


Fig. 4. The measured absorbance for Cr(VI) solution (6 mg/L) as functions of time for a plain solution (without a reagent) and for a solution with a stabilizing reagent. The measurements were performed at the maximum wavelength (~540 nm for the case with a reagent and 371 nm for the case without a reagent) at room temperature.

spectrophotometric analysis with pH. Fig. 5 shows the effect of pH on UV-vis spectra of Cr(VI) solution containing 6 mg/L for the case without a stabilizing reagent. It clear that the spectra of the solutions of Cr(VI) is dependent on pH: both the maximum wavelength and the absorbance vary with the pH of the solution. This factor was ignored in most of the previous adsorption studies, leading to misinterpretation of the adsorption results. The effect of pH on the UV-vis stability of Cr(VI) solutions in the presence 1,5-diphenylcarbazide reagent was also investigated in this study. The pH was first adjusted within the range of 1.6–2.2, since acidic Cr(VI) solution is required in the standard method [30]. Fig. 6 shows the absorbance of the Cr(VI) solution as a function of pH at the maximum wavelength. Although 1,5-diphenylcarbazide was used as a stabilizing reagent, variations in the absorbance values were observed. This indicates instability in the absorbance measurements with changing pH of the solution. These observations indicate that misinterpretation of the adsorption results can be encountered when the pH of the adsorption vessel is changing. Thus, the adjustment the pH of Cr(VI) solution at constant value for all samples is essential for reliable analysis. This issue was not highlighted in the previous adsorption studies [30].

3.3. Adsorption results

The technical feasibility of the treatment of Cr(VI) wastewater by the adsorption onto stone cutting powders was investigated. Fig. 7 shows the kinetic adsorption curve of Cr(VI) solution onto stone cutting particles with an adsorbent dosage of 1 g/100 mL and with an initial Cr(VI) concentration of 60 mg/L at pH = 5 and room temperature (The system was maintained under stagnant conditions, that is, without stirring). Such a general kinetic behavior is in agreement with previous work for adsorbing Cr(III) on the same type of adsorbent (limestone particles) [28]. These results confirm the capability of limestone particles to adsorb Cr(VI) ions. The obtained final removal efficiency

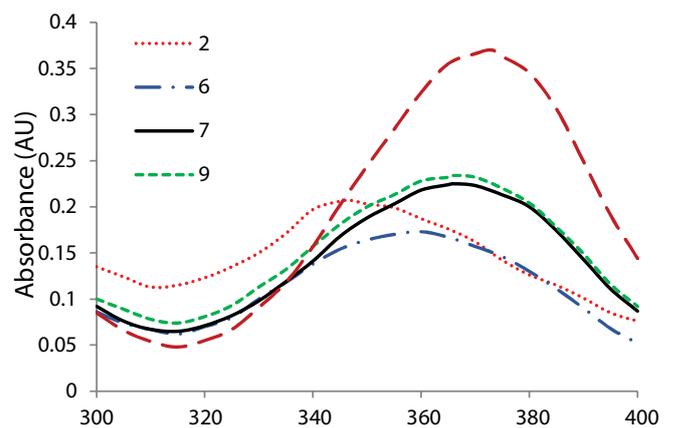


Fig. 5. The effect of pH on the measured spectra for Cr(VI) solution (6 mg/L), without using a reagent at room temperature.

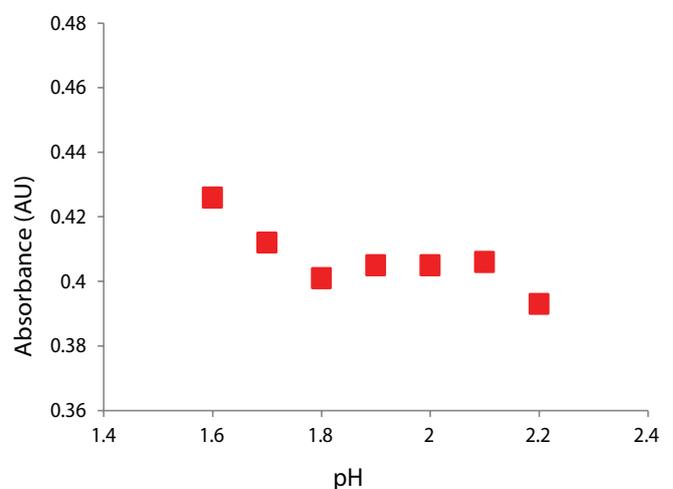


Fig. 6. The measured absorbance at the maximum wavelength for Cr(VI) solution (6 mg/L) with 1,5-diphenylcarbazide reagent as a function of pH at room temperature.

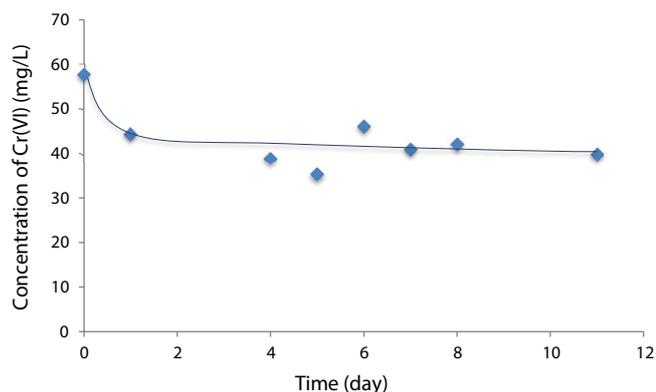


Fig. 7. Adsorption kinetic curve for Cr(VI) solution, with an initial Cr(VI) concentration of 60 mg/L, on stone cutting particles with a dosage of 1 g/100 mL under static condition (without stirring), at a room temperature and pH = 5.

was about 40%. Larger efficiency may be obtained through adjusting experimental parameters, that is, increasing the adsorbent dosage.

4. Conclusions

The results of spectrophotometric measurements of Cr(VI) solution without the use of a stabilizing agent are instable as the absorbance and maximum wavelength of Cr(VI) solution change with time. Stable measurements can be attained after addition of 1,5-diphenylcarbazide to the Cr(VI) solution after 10 min of its preparation. The stability of the system last for only 1 h, after which the absorbance of the solution varies with time and the system becomes instable again. The Cr(VI) can be removed by adsorption onto limestone particles with a removal efficiency of Cr(VI) from the wastewater of about 40% at the applied experimental conditions. The removal efficiency can be significantly improved through adjusting the operating parameters.

The main conclusion of the current study is that Cr(VI) solution suffer from instability of UV-spectrophotometric measurements which can interfere with the actual adsorption results (i.e., percentage removal of pollutant from wastewater) leading to wrong conclusions. Therefore, the addition of a stabilizing agent to the Cr(VI) solutions is essential when UV-spectrophotometric analysis is applied for reliable measurements. The spectrophotometric measurements must be performed within 10–60 min after adding the reagent.

References

- [1] J. Zhu, H. Gu, J. Guo, M. Chen, H. Wei, Z. Luo, H.A. Colorado, N. Yerra, D. Ding, T.C. Ho, Mesoporous magnetic carbon nanocomposite fabrics for highly efficient Cr(VI) removal, *J. Mater. Chem. A*, 2 (2014) 2256–2265.
- [2] B. Qiu, C. Xu, D. Sun, H. Yi, J. Guo, X. Zhang, H. Qu, M. Guerrero, X. Wang, N. Noel, Polyaniline coated ethyl cellulose with improved hexavalent chromium removal, *ACS Sustainable Chem. Eng.*, 2 (2014) 2070–2080.
- [3] C. Xu, B. Qiu, H. Gu, X. Yang, H. Wei, X. Huang, Y. Wang, D. Rutman, D. Cao, S. Bhana, Synergistic interactions between activated carbon fabrics and toxic hexavalent chromium, *ECS J. Solid. State. Technol.*, 3 (2014) M1–M9.
- [4] B. Qiu, C. Xu, D. Sun, H. Wei, X. Zhang, J. Guo, Q. Wang, D. Rutman, Z. Guo, S. Wei, Polyaniline coating on carbon fiber fabrics for improved hexavalent chromium removal, *RSC Adv.*, 4 (2014) 29855–29865.
- [5] S. Langård, Chromium carcinogenicity; a review of experimental animal data, *Sci. Total Environ.*, 71 (1988) 341–350.
- [6] A.K. Mathur, S.V. Chandra, S.K. Tandon, Comparative toxicity of trivalent and hexavalent chromium to rabbits II. Morphological changes in some organs, *Toxicology*, 8 (1977) 53–61.
- [7] A.D. Dayan, A.J. Paine, Mechanisms of chromium toxicity, carcinogenicity and allergenicity: review of the literature from 1985 to 2000, *Hum. Exp. Toxicol.*, 20 (2001) 439–451.
- [8] G.V. Alexeeff, K. Satin, P. Painter, L. Zeise, C. Popejoy, G. Murchison, Chromium carcinogenicity: California strategies, *Sci. Total Environ.*, 86 (1989) 159–168.
- [9] V. Bianchi, A.G. Levis, Review of genetic effects and mechanisms of action of chromium compounds, *Sci. Total Environ.*, 71 (1988) 351–355.
- [10] E. Demirbas, M. Kobya, E. Senturk, T. Ozkan, Adsorption kinetics for the removal of chromium(VI) from aqueous solutions on the activated carbons prepared from agricultural wastes, *Water SA*, 30 (2004) 533–539.
- [11] V.K. Gupta, A. Rastogi, A. Nayak, Adsorption studies on the removal of hexavalent chromium from aqueous solution using a low cost fertilizer industry waste material, *J. Colloid Interface Sci.*, 342 (2010) 135–141.
- [12] J. Hu, G. Chen, I.M. Lo, Removal and recovery of Cr(VI) from wastewater by maghemite nanoparticles, *Water Res.*, 39 (2005) 4528–4536.
- [13] P. Pandey, S. Sharma, S. Sami, Kinetics and equilibrium study of chromium adsorption on zeoliteNaX, *Int. J. Sci. Environ. Technol.*, 7 (2010) 395–404.
- [14] P. Yuan, M. Fan, D. Yang, H. He, D. Liu, A. Yuan, J. Zhu, T. Chen, Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions, *J. Hazard. Mater.*, 166 (2009) 821–829.
- [15] P. Yuan, D. Liu, M. Fan, D. Yang, R. Zhu, F. Ge, J. Zhu, H. He, Removal of hexavalent chromium [Cr(VI)] from aqueous solutions by the diatomite-supported/unsupported magnetite nanoparticles, *J. Hazard. Mater.*, 173 (2010) 614–621.
- [16] H. Shaaalan, M. Sorour, S. Tewfik, Simulation and optimization of a membrane system for chromium recovery from tanning wastes, *Desalination*, 14 (2001) 315–324.
- [17] C.A. Kozłowski, W. Walkowiak, Removal of chromium(VI) from aqueous solutions by polymer inclusion membranes, *Water Res.*, 36 (2002) 4870–4876.
- [18] G. Tiravanti, D. Petruzzelli, R. Passino, Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery, *Water Sci. Technol.*, 36 (1997) 197–207.
- [19] D. Petruzzelli, R. Passino, G. Tiravanti, Ion exchange process for chromium removal and recovery from tannery wastes, *Ind. Eng. Chem. Res.*, 34 (1995) 2612–2617.
- [20] I. Ihsanullah, F.A. Al-Khalidi, B. Abu-Sharkh, A.M. Abulkibash, M.I. Qureshi, T. Laoui, M.A. Atieh, Effect of acid modification on adsorption of hexavalent chromium (Cr(VI)) from aqueous solution by activated carbon and carbon nanotubes, *Desal. Water Treat.*, 57 (2015) 7232–7244.
- [21] D. Sivakumar, Hexavalent chromium removal in a tannery industry wastewater using rice husk silica, *Global J. Environ. Sci. Manage.*, 1 (2015) 27–40.
- [22] T. Chen, Z. Zhou, S. Xu, H. Wang, W. Lu, Adsorption behavior comparison of trivalent and hexavalent chromium on biochar derived from municipal sludge, *Bioresour. Technol.*, 190 (2015) 388–394.
- [23] W. Song, B. Gao, T. Zhang, X. Xu, X. Huang, H. Yu, Q. Yue, High-capacity adsorption of dissolved hexavalent chromium using amine-functionalized magnetic corn stalk composites, *Bioresour. Technol.*, 190 (2015) 550–557.
- [24] N.H. Mthombeni, M.S. Onyango, O. Aoyi, Adsorption of hexavalent chromium onto magnetic natural zeolite-polymer composite, *J. Taiwan Inst. Chem. Eng.*, 50 (2015) 242–251.

- [25] S.S. Baral, S.N. Das, P. Rath, Hexavalent chromium removal from aqueous solution by adsorption on treated sawdust, *Biochem. Eng. J.*, 31 (2006) 216–222.
- [26] M. Jabari, F. Aqra, S. Shahin, A. Khatib, The treatment of chromium tanning wastewater using natural marl, *Chem. Speciation Bioavailability*, 21 (2009) 185–191.
- [27] M. Jabari, F. Aqra, S. Shahin, A. Khatib, Monitoring chromium content in tannery wastewater, *J. Arg. Chem. Soc.*, 97 (2009) 77–87.
- [28] M. Al-Jabari, M. Abualfailat, S. Shaheen, Treating leather tanning wastewater with stone cutting solid waste, *Clean – Soil, Air, Water*, 40 (2012) 206–210.
- [29] H. Sawalha, M. Al-Jabari, I. Tamimi, M. Shahin, Z. Tamimi, Characterization and treatment of wastewater from galvanization industry in Palestine, *Int. J. Environ. Water*, 3 (2016) 37–44.
- [30] L. Clesceri, A. Greenberg, A. Eaton, *Standard Methods for The Examination of Water and Wastewater*, American Water Works Association, 1999.
- [31] M.C. Fournier-Salaün, P. Salaün, Quantitative determination of hexavalent chromium in aqueous solutions by UV-Vis spectrophotometer, *Cent. Eur. J. Chem.*, 5 (2007) 1084–1093.
- [32] L. Di Palma, M.T. Gueye, E. Petrucci, Hexavalent chromium reduction in contaminated soil: A comparison between ferrous sulphate and nanoscale zero-valent iron, *J. Hazard. Mater.*, 281 (2015) 70–76.