



A Comparative Study on Conversion of Soluble Cr(VI) into Insoluble Cr(VI) and Reduction of Cr(VI) in Contaminated Groundwater at COPR Dump Site

VANITHA MURUGAIYAN^{1*}, S. SELVARAJ² and P. KAMATCHI SELVARAJ²

¹Tamilnadu Pollution Control Board, Guindy, Chennai-600032, India

²PG & Research Department of Chemistry, Government Arts College for Men (Autonomous), Nandanam, Chennai-600035, India

*Corresponding author: E-mail: vanithapcb@gmail.com

Received: 1 September 2018;

Accepted: 4 October 2018;

Published online: 31 January 2019;

AJC-19240

The most common methodology for removal of Cr(VI) in literatures is the combination of reduction and precipitation process. The disadvantages of this method are presence of high total dissolved solids in the treated water and sludge generation. In order to find a new solution, efforts have been focussed to convert Cr(VI) present in the groundwater, into the useful products like zinc chromate and barium chromate under appropriate conditions. The efficiency of these conversions is compared with the efficiency of the reduction and precipitation process adopted in this study, using sodium metabisulphite. These experimental studies were carried out with stimulated water containing 2000 mg/L of Cr(VI) and then extended to Cr(VI) contaminated groundwater with same concentration. The results are compared and validated through batch experiments.

Keywords: Contaminated groundwater, Hexavalent chromium, Total chromium, Zinc chromate, Barium chromate.

INTRODUCTION

Industrialization is a basic need for sustained economic growth for developing countries. Amongst the industries, tanneries are the major consumer of chromium over many years for the stabilization of hides. During the past two decades, environmental regulations have become more stringent in improving the quality of treated effluent and remediation of contaminated site [1]. Chromium has a distinctive geochemical behaviour in natural water systems due to redox reaction of Cr(VI) into Cr(III) *vice-versa*. The concentration of chromium in freshwater and seawater is reported to be in the range of 0.1-6.0 µg/L and 2-50 µg/L, respectively [2]. Due to anthropogenic activities, Cr(VI) enter into the environment, exist in aqueous solution in the form of $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , H_2CrO_4 and HCrO_4^- and Cr(III) species as Cr^{3+} , $\text{Cr}(\text{OH})_2^+$, CrO^+ , HCrO_2 and CrO_2^- [3].

The occurrence of higher concentration of Cr is not common due to insolubility of chromite mineral in water [4]. However, significant amount of Cr(VI) was found in surface as well as groundwater due to natural weathering of rocks. This type of contamination has been reported in Sukinda valley of Orissa and Ghaziabad of Uttar Pradesh provinces of India [5]. Samples

collected in similar sources from Calodina, California, Italy and Mexico have been reported up to 73 µg/L and soil in Amazon was in the range of 1864-2346 mg/kg [6].

Apart from mine drainage, the common polluting sources of Cr(VI) are domestic sewage, weathering of mafic or ultramafic rocks and the wastewater generated from industrial applications including electroplating, tanning, textile mordant and dye, industrial water cooling and wood preservation [7]. Contamination due to chromium ore processing residue (COPR) is also a universal problem with significant cases reported in the United Kingdom, United States, Eastern Europe, India, Pakistan and China [8].

In recent years, many techniques such as chemical precipitation, adsorption, membrane filtration, electrodialysis, electrochemical deposition and photo catalysis have been developed for heavy metal removal from contaminated wastewater [9]. Recent study reported that organo-Cr(III) compound is stable in the environment up to 150 °C and the conversion of amorphous organo-Cr(III) into minerals takes place by hydrothermal process, reduces the risk of chromium contamination [10]. The reconversion of Cr(III) species into Cr(VI) species was noticed on aluminium coating due to the presence of dissolved oxygen and

H_2O_2 [11]. Bimetallic Cu Ni nano crystals catalyze is very efficient in the conversion of Cr(VI) to Cr(III) at room temperature in the presence of formic acid [12]. Aghababazadeh *et al.* [13] reported that zinc chromate can be prepared by adding solution of zinc salt and potassium dichromate with NaOH which can be used as a corrosion inhibitor. Beyar and Rieman [14] have reported that a solution containing barium and strontium is separated into barium chromate and strontium chromate by double precipitation. Sodium meta sulfite is a cheap, easily available reducing agent, safe to handle and used as preservative for fruits [15].

In this study, works are executed in three ways in the Cr(VI) contaminated groundwater obtained from COPR site; (i) to obtain zinc chromate, zinc chloride is added in Cr(VI) contaminated groundwater and precipitated with NaOH; (ii) to obtain barium chromate, barium chloride is added in Cr(VI) contaminated groundwater and precipitated with NaOH; and (iii) the contaminated groundwater containing Cr(VI) has been reduced to Cr(III) using sodium metabisulphite in acidic medium and precipitated with NaOH. The influential parameters for the above processes and results are discussed.

EXPERIMENTAL

The chemicals used in this study were of analytical grade and purchased from E-Meerk India Ltd. Synthetic Cr(VI) water was prepared from AR potassium dichromate salt. Barium chloride and zinc chloride were utilized for conversion and sodium metabisulphite was chosen for reduction. Reduction and precipitation were achieved on addition of 1N H_2SO_4 and 1 N NaOH, respectively. Elico pH meter 240 (model L1614) was employed for pH measurement. The initial and residual Cr(VI) concentrations were determined by recording the absorbance at 540 nm using UV-visible spectrophotometer (UV-3200, Lab India). Atomic adsorption spectrometer model Shimadzu 6800 was engaged for accounting total chromium concentration. APHA methods were endorsed to analyse other necessary parameters.

Chromium contaminated ground water (CGW): Ground water contaminated with Cr(VI) piled from the wells located in and around COPR dump site at Ranipet, Vellore district, India was put in to this work. The samples were filtered before subjected to analysis. The electrical conductivity, total dissolved solid and turbidity of the sample containing 2000 mg/L of Cr(VI) were found to be 7580 $\mu\text{s}/\text{cm}$, 5000 mg/L and 195 NTU, respectively.

Synthetic contaminated water (SCW): The SCW was prepared by dissolving 5.658 g of $\text{K}_2\text{Cr}_2\text{O}_7$ in 1000 mL distilled water to have 2000 mg/L of Cr(VI), so as to match it with the concentration of Cr(VI) in contaminated groundwater.

RESULTS AND DISCUSSION

The batch experiments were carried out in two different processes (i) conversion of soluble Cr(VI) in to salts of ZnCrO_4 and BaCrO_4 and (ii) reduction and precipitation of Cr(VI).

Parameters influencing the conversion of Cr(VI) into ZnCrO_4 in SCW: Mirhabibi *et al.* [16] reported that the formation of zinc chromate (yellow pigment) is influenced by the addition of dosage, pH, rotation speed, reaction temperature and stirring time.

Effect of pH on SCW: The initial pH of SCW was recorded at 5.38. In order to find out the effective pH, trial experiments

were executed in SCW by adjusting the pH to 6.5, 7, 8, 9, 10, 11 and 12 using 1 N NaOH. Each trial was carried out in 100 mL of SCW by adding 1 g of zinc chloride and the mixtures were put on magnetic stirrer for 8 h at 280 rpm in room temperature. The precipitates thus obtained were filtered.

Fig. 1 shows the values of Cr(VI) in the filtrates. It is found that Cr(VI) in filtrates were decreased to 1878 mg/L at pH 6.5 and 1256 mg/L at pH 12. Since the maximum conversion was noticed at pH 12, further studies were carried out by adjusting the pH medium to 12 externally.

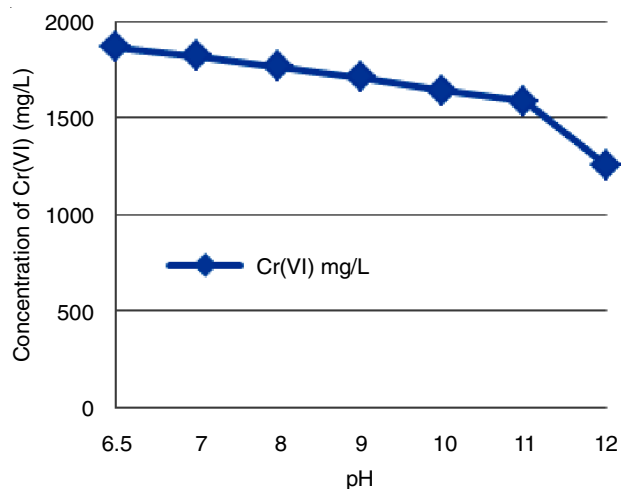


Fig.1. Effect of pH in SCW

Effect of dosage in SCW: Experiments were conducted to analyse the effects of conversion against various dosages of zinc chloride. Since maximum precipitation was occurred in high alkaline medium, studies were executed by varying the dosages of zinc chloride to 1 g, 2 g, 3 g, 4 g and 5 g. The Cr(VI) present in the filtrates were recorded as 1300 mg/L, 639 mg/L, 609 mg/L, 509 mg/L and 492 mg/L, respectively.

From Fig. 2, it is implied that the maximum precipitation was obtained at dosage 3 g. It is apparent evidence that there is no use in merely increasing the dosage of zinc chloride beyond a certain limit. Hence, it was decided to adjust the pH medium to achieve effective conversion. Based on the results obtained in SCW, further experiments were continued in CGW.

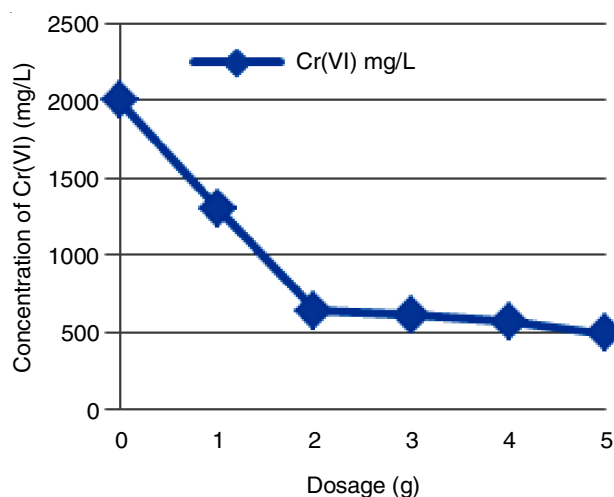


Fig. 2. Level of Cr(VI) in the filtrate after the formation of ZnCrO_4

Effect of dosage, time and precipitation of $ZnCrO_4$ in CGW: Earlier literature has reported that 2 h stirring is not adequate for the formation of zinc chromate [16]. In order to estimate the operational time for the precipitation of $ZnCrO_4$ in CGW, the optimum dosage and pH as obtained in SCW were taken as bench mark (Fig. 3).

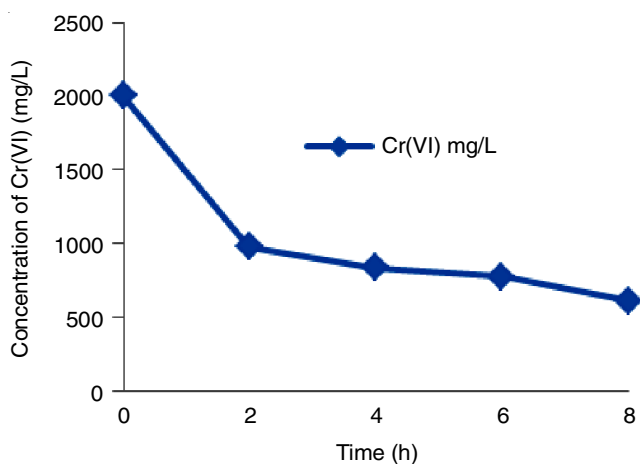


Fig. 3. Effect of time for the formation of $ZnCrO_4$

Effect of time for the formation of $ZnCrO_4$: To 100 mL of CGW, 3 g of zinc chloride was added. Then, the mixture was allowed to run for 1 h, 2 h, 4 h, 6 h and 8 h, and the residual concentration of Cr(VI) in the filtrates were found to be 1267, 1108, 982.5, 868.9 and 673 mg/L, respectively. Even after stirring for 8 h, the conversion of Cr(VI) reached to a level of 66.33 %, which is in agreement with earlier report [13].

X-ray diffraction analysis (Fig. 4) for the precipitated zinc chromate contains diffraction pattern of zinc chromate peaks at 2θ values 32, 45 and 57 and it matches well with the reported value [15].

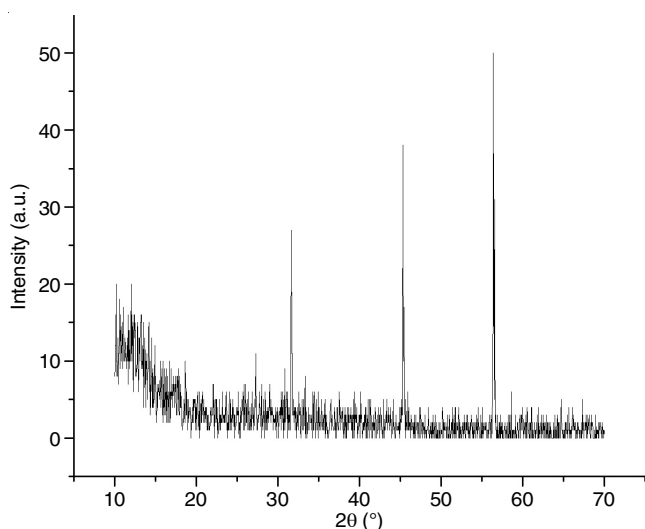


Fig. 4. X-ray diffraction pattern of zinc chromate

Conversion of soluble Cr(VI) into insoluble Cr(VI) in CGW using $BaCl_2$: Attempts were made to find out the suitability of $BaCl_2$ for conversion of $BaCrO_4$. For this conversion 1 g, 2 g and 3 g of $BaCl_2$ was added in 100 mL of CGW and the mixtures were stirred for 0.5 h at room temperature. The

precipitates thus obtained were filtered and the filtrates were analyzed for the determination of Cr(VI). The analyzed reports revealed that considerable amount of Cr(VI) were present in the filtrate at pH 2.1, 1.47 and 1.38 to the respective dosages of 1g, 2 g and 3 g.

Earlier report [16] revealed that the quantitative precipitation of barium chromate occurred at pH 4.6. As the study is focussed to convert all the soluble Cr(VI) into $BaCrO_4$ attempts were made to raise the pH using NaOH. The data observed are shown in Table-1.

Amount of $BaCl_2$ (g)	Initial pH	Adjusted pH	Cr(VI) (mg/L)
1	2.1	–	920
1	–	3.5	725
1	–	4.5	690
1	–	5.0	664
2	1.47	–	123
2	–	2.5	3.42
2	–	3.0	1.67
2	–	3.5	0.89
2	–	4.0	0.0
3	1.38	–	59.2
3	–	2.0	13.8
3	–	2.5	2.27
3	–	3.0	0.00

Table-1 revealed that pH medium was strong acidic on addition of $BaCl_2$ and 100 % removal of Cr(VI) could be noticed in the filtrate at pH 4 for 2 g and pH 3 for 3 g of barium chloride. It was also observed that formation of $BaCrO_4$ occurred rapidly than the formation of $ZnCrO_4$. The XRD recorded for the precipitated $BaCrO_4$ for the dosage of 3 g at pHs 2.5 and 3 are shown in Figs. 5 and 6, respectively. The diffraction peaks appeared around 2θ values 20°, 25°, 28°, 40°, 42°, 48°, 55°, 59° and 65° are in accordance with reported data [17].

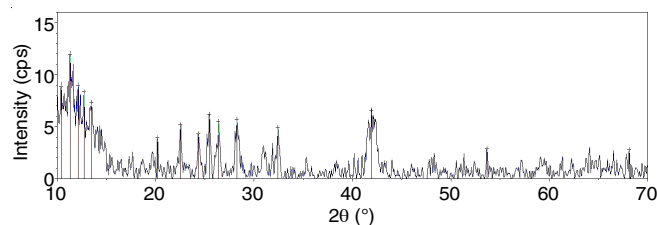


Fig. 5. X-ray diffraction pattern of barium chromate (at pH-2.5)

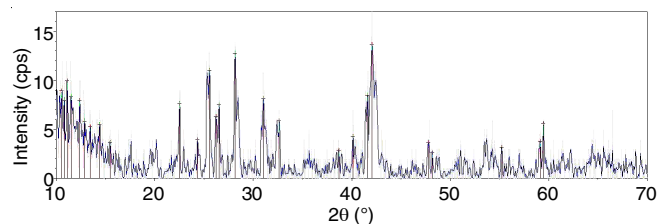


Fig. 6. X-ray diffraction pattern of barium chromate (at pH-3)

Reduction of Cr(VI) into Cr(III): In previous work, the acceptability of sodium dithionite, tin chloride and other reducing agents were discussed [18-20]. Current work employs sodium metabisulphite as reducing agent.

Effect of initial pH, dosage and contact time for SCW:

Removal of Cr(VI) depends on pH of the medium [21]. Different dosage of $\text{Na}_2\text{S}_2\text{O}_5$ (0.06 g, 0.08 g and 0.10 g) were added to 100 mL of SCW. The observed pH of the solutions was in the range of 5.2 to 5.4. The level of Cr(VI) after stirring the mixture continuously for 15, 30, 45 and 60 min were recorded. It is observed that the maximum amount of Cr(VI) is reduced within 15 min time interval (Fig. 7).

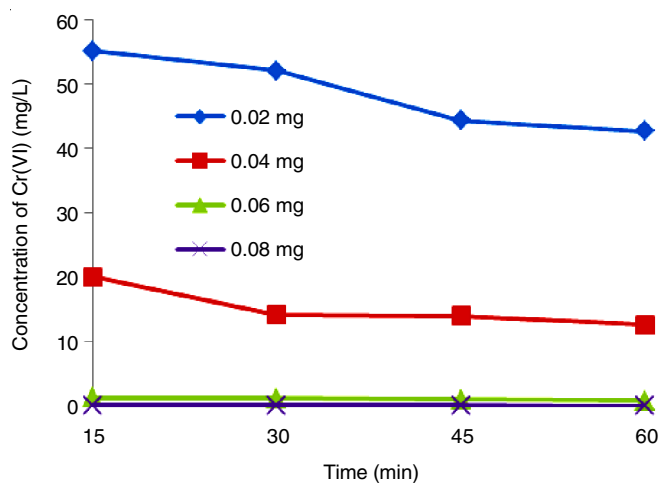


Fig. 7. Reduction of Cr(VI) in SCW without pH adjustment

Study on contaminated groundwater (CGW): Earlier report revealed that pH 9 is the best medium for precipitation [18-22]. In this study, the results obtained in the attempts to evaluate the requirement of $\text{Na}_2\text{S}_2\text{O}_5$ dosage for a CGW sample containing 1800 mg/L of Cr(VI) and 2166 mg/L of total Cr at various reduction pH are presented in Table-2.

Table-2 revealed that pH 3 is the optimum pH for complete reduction of Cr(VI) and pH 9 is the optimum pH for Cr(III)

precipitation. Comparison of results showed that the amount of total chromium is found to be less in pH 2.5 than pH 3 and meet the disposal standard (< 2 mg/L). Further the amount of $\text{Na}_2\text{S}_2\text{O}_5$ consumed at this condition for 100 % reduction of Cr(VI) is the lowest value. The results thus obtained for the conversion of BaCrO_4 , reduction and precipitation process including the presence of parameters such as pH and total dissolved solids (TDS) present in the filtrate are shown in Table-3.

Conclusion

An effort to generate useful material from the hazardous groundwater is met with fruitful results. Even though the amount of chemicals consumed is 2.5 times higher than the reduction and precipitation process, generation of application oriented pigment zinc chromate and barium chromate turns the conventional methods of treating contaminated ground water towards profit oriented process. Lesser consumption of barium chloride and lower requirement of alkali for complete conversion focuses that the salt of barium chromate is better than zinc chromate. However, the filtrate obtained from zinc chromate need further treatment for complete removal of Cr(VI). Apart from that the complications accompanied in the disposal of residue left out in the precipitation process is totally eliminated.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge M/s. Tamilnadu Waste Management Limited, certified by National Accreditation Board for Testing and Calibration Laboratory, SIPCOT Industrial Estate, Gummudipoondi, India for their kind permission to carry out all the analytical studies.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

TABLE-2
EFFECT OF REDUCTION AND PRECIPITATION pH AND DOSAGE OF $\text{Na}_2\text{S}_2\text{O}_5$ ON REDUCTION OF Cr(VI)

Weight of $\text{Na}_2\text{S}_2\text{O}_5$ (g/L)	Reduction at pH-2 and precipitation at pH-9			Reduction at pH-2.5 and precipitation at pH-9			Reduction at pH- 3 and precipitation at pH-9		
	Cr(VI) (mg/L)	Total Cr (mg/L)	Cr(VI) reduction (%)	Cr(VI) (mg/L)	Total Cr (mg/L)	Cr(VI) reduction (%)	Cr(VI) (mg/L)	Total Cr (mg/L)	Cr(VI) reduction (%)
2.0	1009.6	1664.70	43.91	990.85	1670.80	44.95	915.5	1499.4	49.13
4.0	442.0	516.55	75.44	204.4	564.08	88.66	515	1248.5	71.39
6.0	0.0038	4.08	99.88	2.056	2.4848	99.88	126.2	280.4	92.99
8.0	0.0036	2.520	99.99	0.00	0.3686	100	0.00	1.3577	100.00
10.0	0.0422	2.780	99.99	0.00	0.2792	100	0.00	0.7629	100.00

TABLE-3
COMPARISON OF CHEMICALS IN THE REMOVAL PROCESS OF Cr(VI)

Dosage of chemicals used	Optimum pH	Volume of acid/alkali consumed (mL)	Conc. of Cr(VI) in the filtrate (mg/L)	TDS in the filtrate (mg/L)	pH in the filtrate	Chloride in the filtrate (mg/L)
$\text{Na}_2\text{S}_2\text{O}_5$ for reduction (8 g/L)	pH-2.5 for reduction and pH-9 for precipitation	58 mL of 1 N H_2SO_4 for reduction and 106 mL of 1 N NaOH for precipitation	0	8400	7.1	120
BaCl_2 for conversion (20 g/L)	pH-4 for precipitation	21 mL of 1 N NaOH for precipitation	0	6000	5.76	7799
BaCl_2 for conversion (30 g/L)	pH-3 for precipitation	22 mL of 1 N NaOH for precipitation	0	7500	3.6	9926

REFERENCES

1. A. Baral and R.D. Engelken, *Environ. Sci. Policy*, **5**, 121 (2002); [https://doi.org/10.1016/S1462-9011\(02\)00028-X](https://doi.org/10.1016/S1462-9011(02)00028-X).
2. D. Kar, P. Sur, S.K. Mandai, T. Saha and R.K. Kole, *Int. J. Environ. Sci. Technol.*, **5**, 119 (2008); <https://doi.org/10.1007/BF03326004>.
3. S. Loyaux-Lawniczak, P. Lecomte and J. Ehrhardt, *Environ. Sci. Technol.*, **35**, 1350 (2001); <https://doi.org/10.1021/es001073l>.
4. A.D. Apte, V. Tare and P. Bose, *J. Hazard. Mater.*, **128**, 164 (2006); <https://doi.org/10.1016/j.jhazmat.2005.07.057>.
5. L.J.D. Moreira, E.B. da Silva, M.P.F. Fontes, X. Liu and L.Q. Ma, *Environ. Pollut.*, **239**, 384 (2018); <https://doi.org/10.1016/j.envpol.2018.04.025>.
6. M.E. Losi, C. Amrhein and W.T. Frankenberger Jr., *Rev. Environ. Contam. Toxicol.*, **136**, 91 (1994); https://doi.org/10.1007/978-1-4612-2656-7_3.
7. B. Dhal, H.N. Thatoi, N.N. Das and B.D. Pandey, *J. Hazard. Mater.*, **250-251**, 272 (2013); <https://doi.org/10.1016/j.jhazmat.2013.01.048>.
8. C. Su, L.Q. Jiang and W.J. Zhang, *Environ. Skeptics Crit.*, **3**, 24 (2014).
9. M.A. Hashim, S. Mukhopadhyay, J.N. Sahu and B. Sengupta, *J. Environ. Manage.*, **92**, 2355 (2011); <https://doi.org/10.1016/j.jenvman.2011.06.009>.
10. B. Jiang, S. Xin, L. Gao, S. Luo, J. Xue and M. Wu, *Chem. Eng. J.*, **308**, 588 (2017); <https://doi.org/10.1016/j.cej.2016.09.098>.
11. J. Qi, L. Gao, Y. Liu, B. Liu, T. Hashimoto, Z. Wang and G.E. Thompson, *J. Electrochem. Soc.*, **164**, C442 (2017); <https://doi.org/10.1149/2.0021709jes>.
12. B.J. Borah, H. Saikia and P. Bharali, *New J. Chem.*, **38**, 2748 (2014); <https://doi.org/10.1039/c4nj00150h>.
13. R. Aghababzadeh, A.R. Mirhabibi, H. Bastami, E.T. Taheri-Nassaj and L. Lin, *Pigm. Resin Technol.*, **34**, 124 (2004); <https://doi.org/10.1108/03699420510597965>.
14. G.L. Beyer and W. Rieman, *Anal. Chem.*, **19**, 35 (1947); <https://doi.org/10.1021/ac60001a010>.
15. F. Ahmadi, Y.H. Lee, W.H. Lee, Y.K. Oh, K.K. Park and W.S. Kwak, *J. Environ. Manage.*, **224**, 113 (2018); <https://doi.org/10.1016/j.jenvman.2018.07.044>.
16. A.R. Mirhabibi, H. Bastami, E.T. Nassaj, R. Aghababzadeh and L. Lin, *Pigm. Resin Technol.*, **33**, 352 (2004); <https://doi.org/10.1108/03699420410568373>.
17. B. Sinha, A. Dan, A. Wongkamlue, T. Chanakul, S.P. Charinpanitkul, A.K. Moulik and A.K. Panda, *J. Mol. Liq.*, **164**, 171 (2011); <https://doi.org/10.1016/j.molliq.2011.09.004>.
18. A.V. Zubets, L.L. Klimkovich and N.D. Zhigadlo, *Crystallogr. Rep.*, **50**, 1064 (2005); <https://doi.org/10.1134/1.2132418>.
19. V. Murugaiyan, T. Sehar, S. Selvaraj and P.K. Selvaraj, *Asian J. Chem.*, **30**, 620 (2018); <https://doi.org/10.14233/ajchem.2018.21060>.
20. V. Murugaiyan, S. Selvaraj and P.K. Selvaraj, *Orient. J. Chem.*, **34**, 1328 (2018); <https://doi.org/10.13005/ojc/340318>.
21. V. Murugaiyan, S. Selvaraj and P.K. Selvaraj, *Int. J. Appl. Eng. Res.*, **13**, 5265 (2018).
22. G. Wang, Q. Chang, M. Zhang and X. Han, *Reactive Funct. Polym.*, **73**, 1439 (2013); <https://doi.org/10.1016/j.reactfunctpolym.2013.07.009>.