American-Eurasian Journal of Toxicological Sciences 5 (2): 41-47, 2013
ISSN 2079-2050

DOI: 10.5829/idosi.aejts.2013.5.2.1108

Removal of Chromium from Tannery Effluents of Industrial Region District Kasur Punjab

Sheikh Asrar Ahmad and Viqar Un Nisa

Division of Science and Technology, University of Education,
Township Campus Lahore, Postal Code 54590, Pakistan

Abstract: The present work deals with the removal of chromium (VI) from tannery effluents of industrial region of district Kasur Punjab. Chromium (VI) is very toxic metal. It has mutagenic as well as carcinogenic properties. This study was concerned with a low cost-effective approach of removing chromium (VI) from fifteen different samples of tannery effluents collected from the city of Kasur by using bio-sorbent wheat bran. Solutions of various chromium concentrations *viz.,* 21-30 ppm were prepared for calibration. Absorbance was noted using a Spectrophotometer. Tannery effluents samples (KSR1-KSR15) were treated with Wheat Bran (WB). After adsorbent treatment, filtrate was analyzed for the concentration of chromium ions using a UV-Visible Spectrophotometer at 540 nm. The batch system was used to conduct the bio-sorption experiments. The influence of different experimental parameters, such as contact time, pH, amount of adsorbent, was evaluated. Results showed that adsorption of chromium (VI) by wheat bran reached to maximum after 240 minutes. Higher chromium (VI) adsorption was determined at pH 3. Results obtained from the present study were in accordance to international studies.

Key words: Adsorption · Chromium · Tannery · Wheat bran

INTRODUCTION

Chromium is a very toxic metal. It is mutagenic as well as carcinogenic. In addition to that it causes liver damage, lungs infection and skin irritations as reported by Miretzky and Cirelli [1] and Cieslak-Golonka [2] respectively.

According to international standards, permitted limit of Cr (VI) for industrial effluents is 0.1mg dm^{-3}. So the removal of Cr (VI) from industrial effluents is important before discharging. There are various techniques employed for the removal of Cr (VI) i.e. chemical precipitation, coagulation, ion exchange, membrane technologies, adsorption, etc. Many researchers have used different materials to remove Chromium from industrial effluents for example lingo cellulosic agricultural wastes by Krishnani and Ayyappan [3], activated carbon by Dinesh Mohan *et al*. [4], a biomass containing *Streptomyces rimosus* by Junter *et al.* [5], walnut hull by Xue *et al.* [6], an agricultural solid waste (coconut coir pith) by Namasivayam [7], raw agricultural waste by Moussavi and Barikbin [8], modified corn stalks by Suhong Chen *et al*. [9], chitosan/fly ash composite by Wen *et al*. [10], raw dolomite by Albadarin *et al*. [11]. Although these material showed good performance but under Laboratory conditions, their use for large scale effluent treatments was not suitable due to their relatively poor natural abundance as reported by Gao *et al*. [12]. The disadvantage of precipitation was the disposal of the solid waste. Adsorption is very versatile and widely used technique. In the present work an attempt was successfully made to remove chromium VI using wheat bran from tannery effluents of district Kasur, Punjab, Pakistan. Solutions of various chromium concentrations were prepared for calibration. Tannery effluents were treated with Wheat Bran (WB). After giving adsorbent treatment the filtrate was analyzed for the concentration of chromium ions using a UV-Visible Spectrophotometer at 540 nm. The bio-sorption experiments were conducted

Corresponding Author: Sheikh Asrar Ahmad, Division of Science and Technology, University of Education, Township Campus Lahore, Postal Code 54590, Pakistan.

through batch system. The influence of different experimental parameters, such as contact time, pH, amount of adsorbent, was evaluated. Results showed that use of WB is a low cost-effective approach of removing chromium (VI). Removal of Cr (VI) from tannery effluents is beneficial for better crops including fruits, vegetables, wheat rice etc. in agriculture sector.

MATERIALS AND METHODS

Collection of Tannery Waste Samples: A total of 15 industrial effluents were collected from different tanneries located in district Kasur Pakistan. Tannery industrial effluents were named KSR1 to KSR15 accordingly. Table 1 is showing the concentration of chromium in different tannery effluents. District Kasur was selected particularly for this purpose. About 33% of total tanneries in Pakistan were located in district Kasur. PCRWR report showed that a large number of residents of district Kasur were suffering from different diseases due to the presence of Cr in water.

Concentration of Chromium in different tannery waste samples before treatment has been shown in Figure 1.

Adsorbent: The adsorbing material used in this study is wheat bran. It was washed thrice using double distilled water and then dried in an oven at 75°C for one hour. Using pestle and mortar, it was crushed and then sieved to less than 200 mesh size. The surface area of the wheat bran was determined by a three point nitrogen gas adsorption method using a Quantasorb Surface Area Analyzer.

Preparation of Stock Solution: 2.829g of potassium dichromate was dissolved in water to prepare 1000 ppm stock solution of chromium in 100.0 cm^3 of distilled water and then made the volume up to 1 dm^3 with double distilled water.

Preparation of 1% Di Phenyl Carbazide Solution (DPC): One gram of 1, 5 Di Phenyl Carbazide [$CO(NHNHC_6H_5)_2$] was dissolved in acetone followed by addition of a few drops of glacial acetic acid. After that volume up to 100 cm^3 was made by adding acetone in volumetric flask. The solution was stored at very low temperature and was protected from light.

Preparation of 70% Ortho Phosphoric Acid Solution: 70% of ortho phosphoric acid solution was prepared by taking 70 cm^3 of acid and made the volume up to 100 cm^3.

Preparation of 0.05N Sodium Hydroxide Solution: 2.0 g of sodium hydroxide was mixed in distilled water and raised the volume up to 1000 cm^3.

Preparation of 0.5 N Hydrochloric Acid: 43.5 ml of concentrated hydrochloric acid was diluted up to 1000 cm^3 with distilled water.

Preparation of Distilled Water Treated Biosorbent (DWB): Wheat bran was screened and then washed with distilled water till the supernatant layer becomes clear. The washed wheat bran was dried at 105°C in an oven to remove moisture contents.

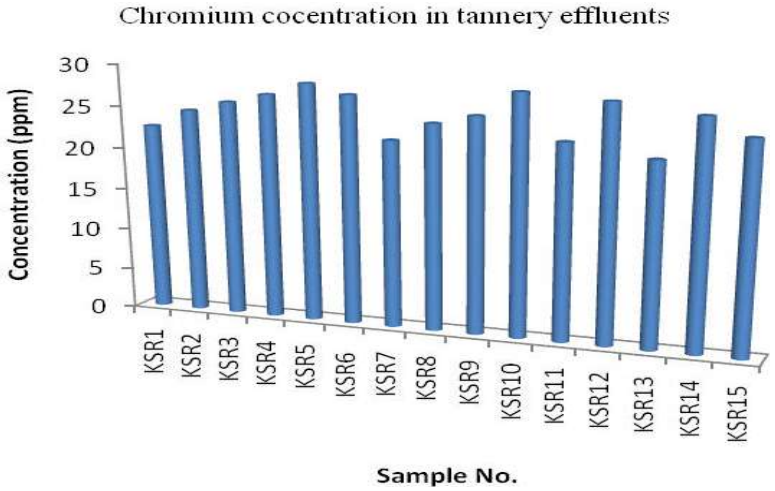

Fig. 1: Concentration of Chromium in different tannery waste samples before treatment

Table 1: Chromium concentration in different waste samples

Sample	Concentration (ppm)	Absorbance (nm)
KSR1	22.5	0.36
KSR2	24.6	0.406
KSR3	25.8	0.433
KSR4	26.9	0.457
KSR5	28.4	0.489
KSR6	27.3	0.472
KSR7	22.3	0.358
KSR8	24.5	0.402
KSR9	25.6	0.429
KSR10	28.5	0.491
KSR11	23.2	0.398
KSR12	27.9	0.479
KSR13	21.8	0.298
KSR14	26.8	0.451
KSR15	24.7	0.429
Average	25.93	

Preparation of Standard Washing Solutions from Stock Solution of Chromium (VI): 1.0 g of pure metal was dissolved in 10.0 cm^3 of conc. HNO_3 and then made the volume 1.0 dm^3 using distilled water to prepare 1000 ppm stock solution. From this stock solution further solutions of 21 to 30 ppm were prepared respectively.

Dilution of Tannery Effluents: The tanning bath was diluted 500 times and treated with 5g wheat bran for 4 hours as reported by Dhabi *et al*. [13].

Calibration Curve: 1.0 ml from each of the above standard solution was taken in 50 ml volumetric flask. Then addition of 1 ml of DPC solution followed by1.0 ml of ortho-phosphoric acid solution to the flask containing 10.0 mL of water. Violet color appeared then raised the volume up to the mark with distilled water. The mixture solution was shaken well. The absorbance measurements of resulting colored solutions were made with Spectrophotometer at 540 nm using against the reagent blank. A graph was plotted between concentration and absorbance. Procedure as same as explained by Singh *et al*. [14].

RESULTS AND DISCUSSION

Di Phenyl Carbazide (DPC) Method: Di Phenyl Carbazide method has been a method of choice of a great number of researchers for example Celik *et al*. [15], Sharma and Forster [16], Dupont and Guillon [17] and Annual book of ASTM Standards [18]. In acid solution, diphenyl carbazide [$CO(NHNHC_6H_5)_2$] forms a soluble red violet product with hexavalent chromium that absorbs light at 540 nm. For all the practical purposes the reaction is specific for chromium, metallic interference almost never occurs. The effect of water color is small and the pH of the solution is not critical. Solution differing by pH 0.7-1.3 gives identical colors. The color of the chromium di phenyl carbazide product changes slightly with time. But for practical purposes it can be considered to be stable. The chromium color develops instantly a de stable.

Determination of Cr (VI): The range of chromium concentration has been reported by Richard *et al*. [19]. The results of concentration of Cr before and after treatment using wheat bran has been shown in Table 2. An average concentration (25.43 ppm) was calculated for all industrial effluents. Maximum concentration was found for sample KSR5 and minimum for sample KSR13. Concentration of Cr in different industrial effluents has been shown in Figure 2.

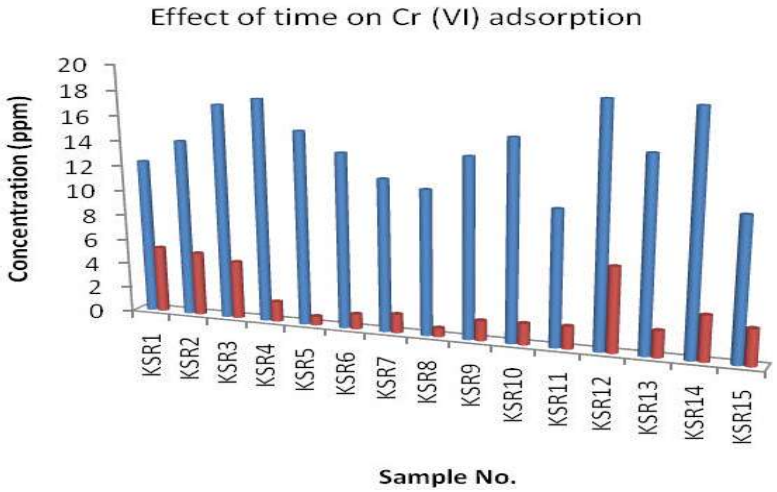

Fig. 2: Effect of Time on Cr (VI) adsorption on wheat bran

DTable 2: Effect of time, pH and amount of adsorbent on chromium adsorption

Sample	CBT (ppm)	CAT (ppm) w.r.t time	Time Min	% age Cr Adsorbed (%) ± SD	CAT (ppm) w.r.t pH	pH	% age Cr Adsorbed (%)±SD	CAT w.r.t A.A (ppm)	AA (g)	% age Cr Adsorbed (%) ± SD
KSR1	22.5	12.38	60	45±0.03	3.37	3	85±0.03	10.24	1	54.5±0.14
		9.9	120	56±0.01	6.75	5	70±0.07	9.67	2	57±0.09
		7.65	180	66.5±0.02	9.11	8	59.5±0.1	5.17	4	77±0.01
		5.29	240	76.5±0.01	14.2	10	36.8±0.14	4.27	5	81±0.06
KSR2	24.6	14.02	60	43±0.1	2.98	3	87.9±0.18	11.4	1	53.6±0.04
		9.89	120	59.8±0.05	6.69	5	72.8±0.17	9.8	2	60.1±0.06
		7.12	180	71.0±0.04	9.59	8	61±0.2	5.1	4	79.2±0.10
		5.07	240	79.4±0.01	14.3	10	41.8±0.13	3.9	5	84.1±0.13
KSR3	25.8	17.13	60	33.6±0.01	2.76	3	89.3±0.01	10.6	1	58.9±0.01
		11.99	120	53.5±0.02	6.45	5	75±0.03	9.31	2	63.9±0.02
		7.22	180	72±0.07	9.54	8	63±0.04	6.71	4	74±0.08
		4.62	240	82.1±0.05	11.3	10	56.2±0.12	5.77	5	78±0.09
KSR4	26.9	17.75	60	34±0.01	1.88	3	93±0.14	10.49	1	61±0.04
		12.37	120	54±0.05	6.21	5	76.9±0.12	9.15	2	66±0.12
		10.36	180	61.5±0.01	9.28	8	65.5±0.11	6.45	4	76±0.18
		1.61	240	94±0.03	12.4	10	53.9±0.15	5.38	5	80±0.07
KSR5	28.4	15.45	60	45.6±0.01	1.42	3	95±0.1	3.52	1	87.6±0.13
		14.2	120	50±0.03	6.24	5	78±0.11	2.55	2	91±0.17
		7.87	180	72.3±0.06	9.37	8	67±0.19	0.96	4	96.6±0.10
		0.71	240	97.5±0.02	14.1	10	50.3±0.23	0.45	5	98.4±0.12
KSR6	27.3	13.9	60	49.0±0.03	2.4	3	91.2±0.21	16.7	1	38.8±0.09
		10.6	120	61.1±0.03	7.8	5	71.4±0.25	14.2	2	47.9±0.03
		5.1	180	81.3±0.01	10.3	8	62.2±0.21	7.2	4	73.6±0.02
		1.2	240	95.6±0.01	12.9	10	52.7±0.18	6.1	5	77.6±0.10
KSR7	22.3	12.1	60	45.7±0.08	4.2	3	81.1±0.11	7.6	1	65.9±0.04
		8.5	120	61.8±0.09	6.7	5	69.9±0.04	4.5	2	79.8±0.05
		3.6	180	83.8±0.1	7.5	8	66.7±0.02	2.9	4	86.9±0.09
		1.5	240	93.2±0.12	9.4	10	57.8±0.01	2.6	5	88.3±0.07
KSR8	24.5	11.5	60	53.0±0.01	5.6	3	77.1±0.06	10.7	1	56.3±0.01
		7.6	120	68.9±0.07	8.3	5	66.1±0.14	9.1	2	62,8±0.01
		2.9	180	88.1±0.15	10.2	8	58.3±0.09	2.2	4	91±0.03
		0.7	240	97.1±0.21	13.1	10	46.5±0.21	1.9	5	92.2±0.07
KSR9	25.6	14.2	60	44.5±0.07	2.3	3	91±0.02	13.4	1	47.6±0.03
		11.3	120	55.8±0.41	5.7	5	77.7±0.01	9.2	2	64±0.09
		9.5	180	82.4±0.02	9.2	8	64±0.07	3.4	4	86.7±0.10
		1.6	240	93.7±0.07	11.1	10	56±0.11	2.2	5	91.4±0.11
KSR10	28.5	15.8	60	44.5±0.02	4.6	3	83.8±0.31	12.6	1	55.7±0.11
		9.7	120	65.9±0.06	7.2	5	74.7±0.23	9.7	2	65.9±0.16
		4.3	180	84.9±0.1	9.1	8	68±0.09	1.2	4	95.7±0.08
		1.7	240	94.0±0.11	10.5	10	63.1±0.12	1.1	5	96.1±0.14
KSR11	23.2	10.7	60	53.8±0.08	3.7	3	84±0.07	15.3	1	34±0.06
		6.2	120	73.2±0.09	6.8	5	70.6±0.02	12.4	2	46.5±0.12
		2.4	180	89.6±0.1	9.8	8	57.7±0.02	8.4	4	63.7±0.04
		1.8	240	92.2±0.01	13.2	10	43.1±0.07	6.2	5	73.2±0.03
KSR12	27.9	18.9	60	32.2±0.08	4.4	3	84.2±0.04	14.3	1	48.7±0.06
		17.5	120	37.2±0.04	6.7	5	75.9±0.03	10.5	2	62.3±0.01
		12.8	180	54.1±0.03	9.3	8	66.6±0.06	6.3	4	77.4±0.01
		6.7	240	75.9±0.01	14.5	10	48±0.01	4.1	5	85.3±0.03
KSR13	21.8	15.2	60	30.2±0.06	5.2	3	76.1±0.02	13.7	1	31.1±0.01
		11.4	120	47.7±0.11	7.3	5	66.5±0.04	10.1	2	53.6±0.06
		6.3	180	71.1±0.23	10.1		53.6±0.05	6.5	4	70.1±0.06
		2.1	240	90.3±0.32	12.7	8	41.7±0.02	5.2	5	76.1±0.03

Table 2: Continue

KSR14	26.8	18.7	60	30.2±0.9	4.1	3	84.7±0.09	16.2	1	39.5±0.02
		14.9	120	44.4±0.8	6.9	5	74.2±0.12	13.8	2	48.5±0.11
		7.5	180	72.0±1.03	9.8	8	63.4±0.11	7.4	4	72.3±0.14
		3.6	240	86.5±0.81	13.4	10	50±0.22	5.6	5	79.1±0.13
KSR15	24-7	11.2	60	54.6±0.04	3.4	3	86.2±0.13	15.1	1	38.8±0.08
		6.9	120	72.0±0.31	6.7	5	72.8±0.14	13	2	47.3±0.06
		3.2	180	87.0±1.07	9.9	8	59.9±0.11	6.7	4	72.8±0.06
		2.9	240	88.2±0.81	12.8	10	48.1±0.1	4.5	5	81.7±0.03

C. B. T: Concentration Before Treatment; C. A. T: Concentration After Treatment; A.A: Amount of Adsorbent; w.r.t: With Reference To; ppm: Parts Per Million; S.D: Standard Deviation

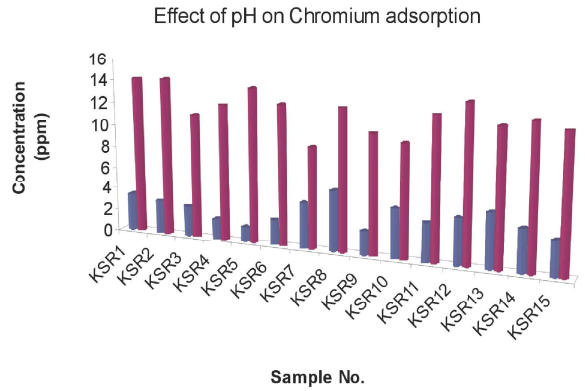

Fig. 3: Effect of pH on Cr (VI) adsorption on wheat bran

Effect of Time on Chromium Adsorption Using Wheat Bran: Moussavi *et al*. [9] reported that Pistachio Hull Powder (PHP) in acidic medium adsorbed about 99% Cr from aqueous solution in sixty minutes. Since industrial effluents were complex material so a long time up to 240 minutes was given to all 15 samples. Concentration of Cr was determined at four intervals of 60 minute time. Table 2 explains the effect of time on chromium adsorption using wheat bran. An average concentration of Cr after treatment was 9.8 ppm in an average time of 150 minutes with an average of 62.36 % adsorbed Cr. Maximum percentage of Cr adsorbed was found for KSR5 (97.5%) after 240 minutes and minimum (30.2%) for KSR 13 in 60 minutes.

Effect of pH: pH of an aqueous solution has effect on adsorption of Cr using WB. The effect of the time on chromium adsorption using wheat bran has been shown in Figure 3. The presence of hydroxyl groups has been confirmed in the residues of wheat bran and rice straw as reported by Dupont *et al*. [17]. Xue *et al*. [6] studied the removal of Cr (VI) from an aqueous solution by using walnut hull. He concluded that removal of Cr (VI) was pH dependent. About 97.3% Cr (VI) was removed at pH 1.0. While Moussavi *et al*. [7], removed 99.0% Cr (VI) by adsorbing on PHP at pH 2.0. Ahmad *et al*. [11] used raw dolomite in batch adsorption experiments removed maximum Cr (VI) at pH 2.0.

Niladri *et al*. [20] efficiently removed chromium (VI) using glycine doped poly pyrrole adsorbent from aqueous solution. Adsorption of Cr (VI) onto the PPy-glyadsorbent was highly pH dependent. In literature maximum adsorption of Cr (VI) using different adsorbents has been reported at pH 1-2. In present work effect of pH on Cr adsorption using wheat bran has been studied at pH 3.0, 5.0, 8.0 and 10.0 respectively. The results as shown in Table 2 showed that lower pH 3.0 favor the maximum Cr (VI) adsorption on wheat bran as compared to pH 10.0. Maximum adsorption (95.0%) of Cr (VI) was noted for industrial effluents, KSR5 at pH 3.0 and minimum adsorption (36.8%) for KSR1. An average (67.74%) Cr adsorption was noted at pH 6.5.

Park [21] in 2006 reduced Cr (VI) easily to Cr (III) when in by contact with organic materials under acidic conditions.

Wheat Bran as Chromium Adsorbent: Wheat bran was an easily available, low cost and simple processed material (as agricultural product). WB does not only clean the Cr from the contaminated water but also removes other toxic metals like lead.

Effect of Amount of Adsorbent on Cr (VI): Gholamreza *et al*. [8] used PHP as adsorbent in concentration of 0.5-0.8 g/ dm^3 for removal of Cr (VI) from aqueous solution. In the present study, chromium concentration in different waste samples is shown in Table 1 while different amounts of adsorbent i.e., 1.0, 2.0, 4.0 and 5.0 g/dm^3 were taken respectively to study the Cr adsorption before and after treatment as given in Table 2. In general, it was found that percentage of Cr adsorption increased gradually with the increase of the amount of adsorbent. Greater amount of adsorbent offers the larger contact area for adsorbants. The effect of amount of

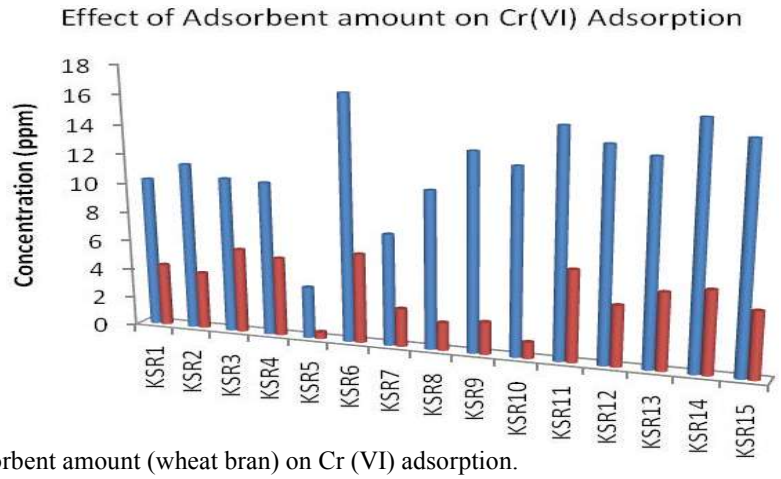

Fig. 4: Effect of adsorbent amount (wheat bran) on Cr (VI) adsorption.

adsorbent on chromium adsorption using wheat bran has been shown in Figure 4. Maximum percentage of adsorbed Cr (98.4%) was noted for the sample KSR5 and minimum (31.1%) for KSR13.

ACKNOWLEDGEMENTS

Authors specially thank to Pakistan Council of Science and Industrial Research Ferozpur Road Lahore, Pakistan for providing research facilities.

REFERENCES

1. Miretzky, P. and A.F. Cirelli, 2010. Cr (VI) and Cr (III) removal from aqueous solution by raw and modified lignocellulosic materials: A review, J. Haz. Mat., 180(1-3): 1-19.
2. Cieslak, M. and Golonka, 1996. Toxic and mutagenic effects of chromium (VI), Polyhedron, 15: 3667-3918.
3. Krishnani, K.K. and S. Ayyappan, 2006. Heavy metals remediation of water using plants and lingo cellulosic agro wastes, Rev. Environ. Contam. Toxicol., 188: 59-84.
4. Dinesh, M. and Charles U. Pittman Jr, 2006. Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water, J.Haz. Mat., 137(2): 762-811.
5. Junter, G.A., A. Chergui, M.Z. Bakhti, A. Chahboub, S. Haddoum and A. Selatnia, 2007. Simultaneous biosorption of Cu^{2+}, Zn^{2+} and Cr^{6+} from aqueous solution by Streptomyces rimosus biomass, Desalination, 206(1-3): 179-184.
6. Xue Song Wang, ZhiZhong Li and Sheng Rong Tao, 2009. Removal of chromium (VI) from aqueous solution using walnut hull, Journal of Environmental Management, 90(2): 721-729.
7. Namasivayam, C. and M.V. Sureshkumar, 2008. Removal of chromium (VI) from water and wastewater using surfactant modified coconut coir pith as a biosorbent, Bioresource Technology, 99(7): 2218-2225.
8. Gholamreza, M. and Behnam Barikbin, 2010. Biosorption of chromium(VI) from industrial wastewater onto pistachio hull waste biomass, Chemical Eng. J., 162(3): 893-900.
9. Suhong, C., QinyanYue, Baoyu Gao, Qian Li and Xing Xu, 2011. Removal of Cr (VI) from aqueous solution using modified corn stalks: Characteristic, equilibrium, kinetic and thermodynamic study, Chem. Eng. J., 168(2): 909-917.
10. Yue Wen, Zhiru, Tang, Yi Chen and Yuexia Gu, 2011. Adsorption of Cr(VI) from aqueous solutions using chitosan-coated fly ash composite as biosorbent, Chem. Eng. J., 175: 110-116.
11. Ahmad, B. Albadarin, Chirangano Mangwandi, Ala'a H. Al-Muhtaseb, Gavin M. Walker, Stephen J. Allen and Mohammad N.M. Ahmad, 2012. Kinetic and thermodynamics of chromium ions adsorption onto low-cost dolomite adsorbent, Chem. Eng. J., 179: 193-202.
12. Gao, H., Y. Liu, G. Zeng, W. Xu, T. Li and W. Xia, 2008. Characterization of Cr(VI) removal from aqueous solutions by a surplus agricultural waste-rice straw, J. Haz. Mat., 150: 446-452.
13. Dhabi, S., M. Azzi and M. De la Gardia, 1999. Removal of hexavalent chromium from industrial effluents by bone charcoal, Fresenius J. Anal.Chem, 303: 404-407.
14. Singh, K.K., S.H. Hasan, M. Talat, V.K. Singh and S.K. Gangwar, 2009. Removal of Cr (VI) from aqueous solutions using wheat bran, Chem. Eng. J., 151(1-3): 113-121.

15. Celik, A., K. Dost and H. Sezer, 2004. An investigation of Chromium (VI) ion removal from wastewaters by adsorption on residual lignin, Fresenius Environ. Bull., 13: 124-127.
16. Sharma, D.C. and C.F. Forster, 1994. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents, Bioresour. Technol., 47: 257-264.
17. Dupont, L. and E. Guillon, 2003. Removal of hexavalent chromium with a lignocellulosic substrate extracted from wheat bran, Environ. Sci. Technol., 37: 4235-4241.
18. ASTM., 2009. Annual Book of ASTM Standards, 'Standard Test Methods for Chromium in Water', D1687-02R07E01, 11.01, 2009.
19. Richard, F. and A. Bourg, 1991. Aqueous geochemistry of chromium: a review, Water Res., 25: 807-816.
20. Niladri Ballav, ArjunMaity, Shivani and B. Mishra, 2012. High efficient removal of chromium(VI) using glycine doped polypyrrole adsorbent from aqueous solution, Chemical Engineering Journal, 198-199, pp: 1-5.
21. Park D., Yeoung-Sang Yun and Jong Moon Park, 2006. Mechanisms of the removal of hexavalent chromium by biomaterials or biomaterial-based activated carbons, J. Haz. Mat., 137(2): 1254-1257.