International Journal of Advance Research in Science and Engineering
Vol. No.6, Issue No. 04, April 2017
www.ijarse.com
IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

REMOVAL OF CHROMIUM FROM INDUSTRIAL EFFLUENT BY ADSORPTION USING ALUMINA SILICA MONOLITH

V.R. Doss[1], Manik Gondhali[2], S. Jain[3],

[1]Associate Professor, Department of Engineering Sciences, Sinhgad College of Engineering, Vadgaon (Bk.), Pune (India)

[2]Post-Graduate Student, [3]Associate Professor, Department of Civil (Environmental) Engineering, Sinhgad College of Engineering, Vadgaon(Bk.), Pune (India)

ABSTRACT

Electroplating industry contains chromium in its effluent. The present study aims at using silica monoliths as an adsorbent to remove chromium from wastewater of electroplating industry. Four different Isotherm models Langmuir, Freundlich, Temkin and Dubunin – Radushkevich were validated. Langmuir model showed the best fit with an R^2 *value of 0.9282. Batch kinetic experiments were conducted to examine the effect of various parameters like initial metal ion concentration, contact time, pH and temperature.7 g/100 ml of adsorbent shows efficient removal upto 90.47% at an optimum pH of 4 in a period of 150 minutes. The functional acidic sites on the mesoporous monoliths provide effective and accessible adsorption of metal ions.*

Keywords: adsorption, Isotherms, Alumina Silica Monoliths.

I. INTRODUCTION

Electroplating waste is one of the major contributors to heavy metal pollution in surface waters. A large number of heavy metals are generated annually by industrial activity that has contaminated water bodies all over the world. Therefore, heavy metal pollution has received much attention in the media and scientific literature due to the severe toxic effects on human health and the environment. The important toxic metals like Cd, Zn, Pb, Ni, Cr, Cu and Hg enter into the water bodies through waste water from metal plating industries and industries of Cd- batteries, mining, pigments, stabilizers alloys etc.In the top 50 priority list for toxic substances Chromium (Cr) is one of the eight metals (ATSDR 2003). Cr(III) is usually benign due to poor membrane permeability [1]. Trivalent compounds are poorly absorbed by the gastrointestinal tract hence have low toxicity as compared to hexavalent chromium. Cr (VI) is a skin and mucous membrane irritant. Hexavalent chromium is considered as a potential pulmonary carcinogen. Low-level occupational chromium exposure induced DNA damage in electroplating workers[2].

For the removal of heavy metals from effluent waste streams the adsorption process with various commercial and natural adsorbents like F-400 activated carbon, Apricot stone, corn cob, rice bran, etc. are being widely used[3-17]. Such adsorbent remains an expensive material or one with surface limitations thus, the use of alternative and perhaps cheaper adsorbents with well- defined surface characteristics is attractive. Mesoporous monoliths have distinctive properties which categorize them as a promising material for removal of organic and inorganic pollutants [18-24].

II. MATERIALS AND METHOD

2.1 Characterization of the adsorbent

The alumina silica monolith procured from m/s Shilpa enterprises, Nagpur was subjected to SEM, XRD and FTIR analysis. SEM micrograph gives a characteristic three dimensional appearance useful for understanding the surface structure of a sample. SEM was carried out on JULJSM – 6360A and the results are shown in Fig 1(A) and (B). XRD for the alumina silica monolith both before and after adsorption were carried out on Bruker AXS D8 Advanced as shown in Fig 2 (A) and (B). FTIR showing surface functional groups was carried out on Perkin Elmer, FT-IR system, Spectrum BX; shown in Fig 3 (A) and (B). The EDS report is shown in Fig 4.

2.2 Physico-chemical analysis of the electroplating wastewater

The sampling and analysis of various physico-chemical properties has been done to understand the composition of electroplating industry effluent. The effluent samples were collected from the Electroplating industry, S. V. Metal Finishers Pvt. Ltd, Dhayari Pune, Maharashtra, India. The sample bottles were filled, labelled and transported to the laboratory, stored and physico-chemical analysis of the samples were done. The results of which are shown in Table.1

2.3 Experimental Procedure

Batch adsorption and kinetic experiments were carried out to validate the isotherm models and study the effect of initial metal ion concentration, contact time, pH and temperature on the adsorption of Cr on the Alumina Silica monolith.

2.3.1 Adsorption Isotherm Studies

This was carried out to study the adsorbing capacity of adsorbent in a fixed quantity of solution with varying adsorbent quantity. This parameter gives the optimum amount of adsorbent required. 100 ml of hexavalent chromium sample was taken in a beaker. Varying amounts of 0.5 g to 15 g of alumina silica monolith was added in different beakers. To this was added 10 ml diphenyl carbazide. Beakers were then placed on a magnetic stirrer at moderate speed which was set at a room temperature of 30°C. Samples were stirred for 8 hrs. The amount of the adsorbate per unit mass of the adsorbent i.e. q_e in mmol/g of the molecules at equilibrium was determined using the equation,

$$q_e = C_0 - C_e \times V/W$$

Where q_{e}- amount of the adsorbate per unit mass of the adsorbent
V- Volume of solution in liters
C_0 and C_e are initial and equilibrium concentration of adsorbent
W- Amount of adsorbent in g

The isotherms were validated for Langmuir, Freundlich, Temkin and Dubunin-Radushkevich isotherms as shown in Fig 5-8.

2.3.2 Kinetic studies

2.3.2.1 Variation of dose

This parameter gives the optimum dose of adsorbent for maximum % Cr (VI) removal efficiency. To 100 ml of hexavalent chromium sample, 1-8 g of the adsorbent was added along with 10 ml diphenylcarbazide. Beaker was then placed on a magnetic stirrer at moderate speed which was set at room temperature of 30^{o}C. After 4 hours sample was filtered and analyzed. Same procedure was followed for pH 2 and 9. The % Cr (VI) removal efficiency vs. adsorbent dosage is shown in Fig 9.

2.3.2.2 Variation of temperature

This study was carried out to study the effect of temperature on the adsorbing capacity of the adsorbent. 100 ml of hexavalent chromium sample was taken in beaker. To this 1 gm of silica alumina monolith and 10 ml diphenylcarbazide was added. Samples were stirred for 4 hours at room temperature of 30^{o}C. Similarly, the procedure was repeated for 15^{o}C and 40^{o}C. After completion of different runs, samples were filtered and analyzed using AAS Chemito AA 201. The results are shown in Fig 10.

2.3.2.3 Variation of contact time

The adsorption of the Alumina silica monolith was studied at various time intervals (0-180 min). Kinetic sorption studies were carried out using 500 ml of the sample with adsorbent dose of 5 g with 10 ml diphenylcarbazide. The mixture was uniformly agitated at 30°C for 15 minutes. The experimental setup is thereafter repeated for various time intervals of 30, 45, 60, 90, 120, 150, 180 and 240 minutes. The concentration of metal ions in the filtrates is determined using AAS as shown in Fig 11.

2.3.2.4 Variation of pH

This parameter gives the optimum pH to get maximum % Cr (VI) removal efficiency. 100 ml of hexavalent chromium sample having a pH of 7 were taken in a beaker and to this 1 g of the adsorbent was added along with 10 ml diphenyl carbazide. Beaker was then placed on a magnetic stirrer at moderate speed which was set at room temperature of 30^{o}C. After 4 hours sample was filtered and analyzed. Same procedure was followed for pH 2 and 9. The % Cr (VI) removal efficiency vs. pH is shown in Fig 12.

2.3.2.5 Agitation speed

This was carried out to study the adsorbing capacity of the adsorbent by varying the speed of agitation to get maximum % removal efficiency of Cr (VI). 100 ml of hexavalent chromium sample was taken in beaker.To this 1 g of alumina silica monolith and 10 ml diphenyl carbazide was added. Speed of agitation was kept at 200, 600 and 1000 rpm. After 6 hours sample was filtered and analysed in AAS. This gives graph of Cr (VI) removal efficiency in percentage vs. Agitation (rpm) as shown in Fig13.

III. RESULTS AND DISCUSSION

3.1 Characterization of the adsorbent

Surface texture analysis was carried out using a Scanning Electron Microscope. SEM of alumina silica monolith before adsorption shows a porous surface texture while after adsorption shows adsorbed chromium on the surface.

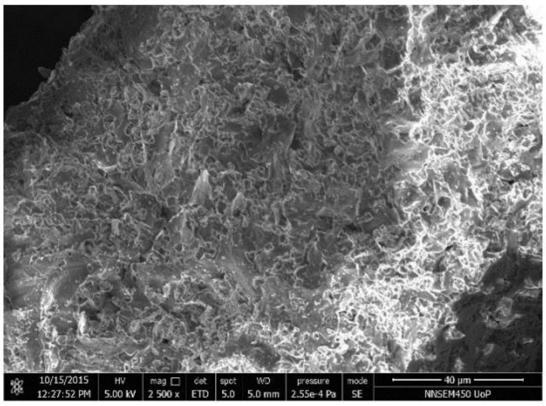


Fig 1 (A) Before adsorption

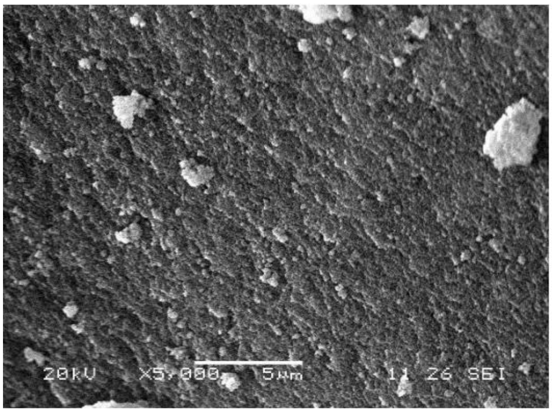


Fig 1 (B) After adsorption

XRD of the adsorbent shows variations in the characteristic peaks relating to interplanar spacings in the adsorbent before and after adsorption.

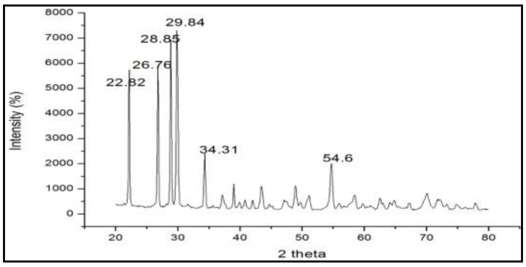


Fig 2 (A) XRD Before adsorption

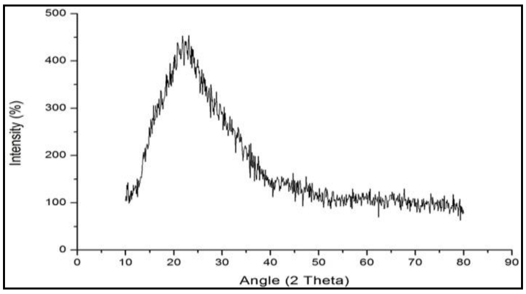


Fig 2 (b) XRD After adsorption

The FTIR spectrum obtained for alumina silica monolith is presented below. The IR band at 3434 cm^{-1} is due to the stretching vibration of H_2O while the band at 1631 cm^{-1} is due to the bending vibration of H_2O. A strong band at 1206 cm^{-1} with a shoulder at 1179 cm^{-1} is assigned due to modes of Si-O-Si stretch vibrations. Bands at 1066 cm^{-1} and 802 cm^{-1} are also due to Si-O-Si stretch vibrations. The IR band at 949 cm^{-1} can be assigned to silanol group. At 808 cm^{-1} it is due to Si-O-Si symmetric stretch and at 483 cm^{-1} due to O-Si-O bend vibration. The bands that were observed between 400 cm^{-1} – 850 cm^{-1} were due to Al-O stretching. At 447 cm^{-1}, 576 cm^{-1} and 676 cm^{-1} and 767 cm^{-1} it is due to Al-O stretch vibrations.

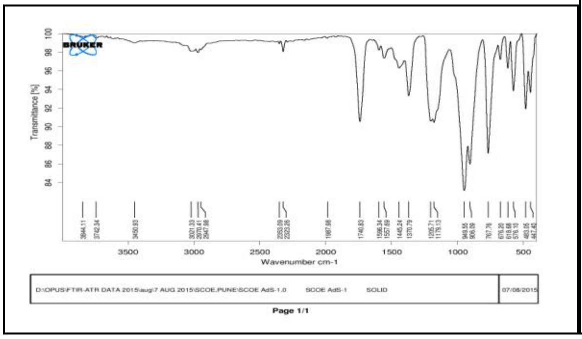


Fig 3 (A) FTIR Before adsorption

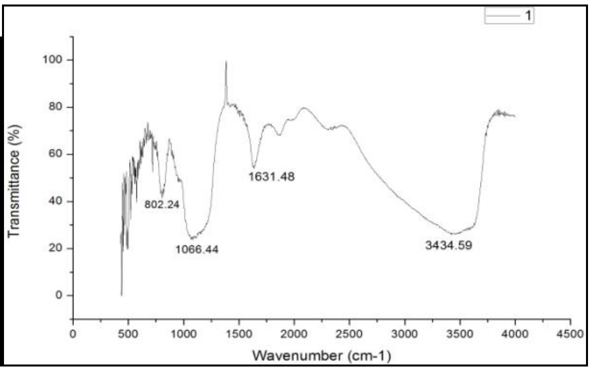
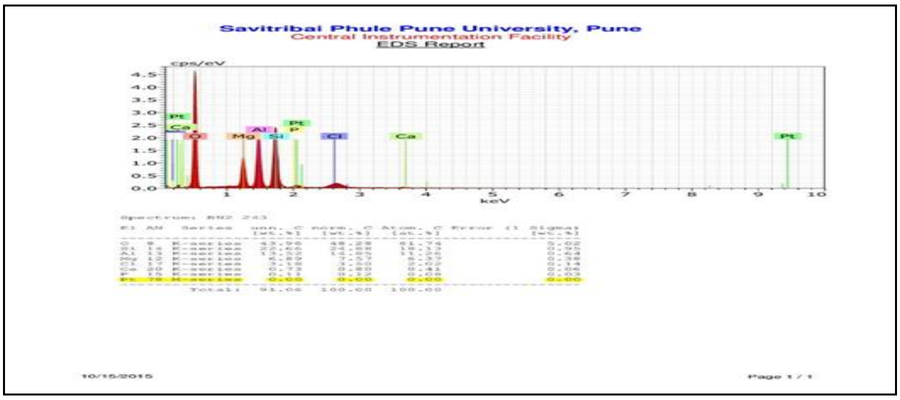


Fig 3 (B) FTIR After adsorption

The EDS shows presence of Oxygen, Silicon and Aluminium in the adsorbent as the major elements present.



Savitribai Phule Pune University, Pune
Central Instrumentation Facility
EDS Report

```
Spectrum: BN2 243

El AN  Series   unn. C  norm. C  Atom. C  Error (1 Sigma)
                [wt.%]  [wt.%]   [at.%]          [wt.%]
-----------------------------------------------------------
O   8  K-series  43.96   48.28    61.74            5.02
Si 14  K-series  22.66   24.88    18.13            0.95
Al 13  K-series  13.52   14.85    11.26            0.64
Mg 12  K-series   6.89    7.57     6.37            0.38
Cl 17  K-series   3.18    3.50     2.02            0.14
Ca 20  K-series   0.73    0.80     0.41            0.06
P  15  K-series   0.11    0.12     0.08            0.03
Pt 78  M-series   0.00    0.00     0.00            0.00
-----------------------------------------------------------
        Total:   91.06  100.00   100.00
```

10/15/2015

Page 1 / 1

Fig 4 EDS of silica alumina monolith

3.2 The physico-chemical analysis of the wastewater is shown in the Table below

Parameters	Standard values*	Experimental values
pH	6-9	1.66
Temperature	Ambient Temp +5^{0}C	32^{0}C
Oil and grease	10	4.6
Suspended solids	100	12
cyanides	0.2	-
Ammonical Nitrogen	50	7.5
Total residual Chlorine	1	0.54
Cd	2	-
Ni	3	18.2
Zn	5	-
Cr	**0.1**	**194.33 ppm**
COD	-	486
Cu	3	4.9
Pb	0.1	3.8
Fe	3	-
Total metal	10	221.3

*Standards for emission of pollutants from various industries, CPCB, Ministry of Env. AndForests, GOI.

3.3 Adsorption Isotherm studies

The Langmuir isotherm model with R^2 value of 0.9282 was found to be the best fit of all the models validated.

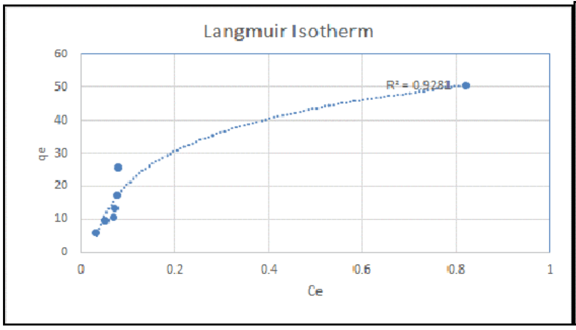


Fig 5- Langmuir isotherm

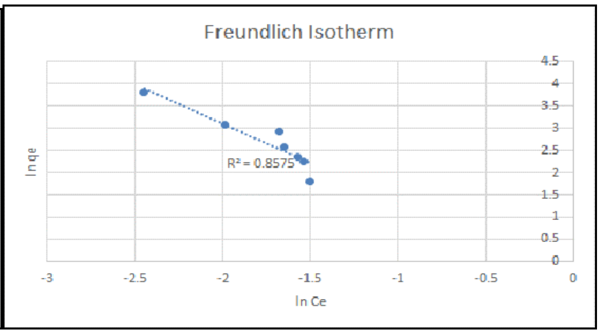


Fig 6-Freundlich isotherm

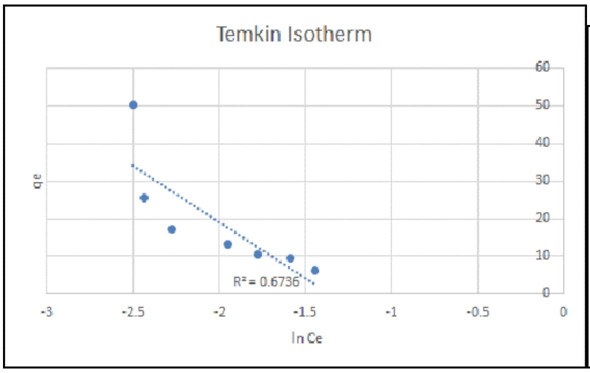


Fig 7-Temkin isotherm

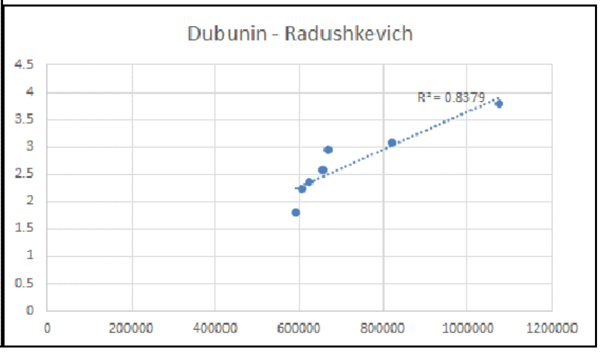


Fig 8-Dubunin- Radushkevich isotherm

3.4 Effect of Dose Variation

Following results were obtained for variation of dose which shows maximum % removal for 7 mg of the adsorbent. This shows that the adsorption increases with increase in adsorption dosage but once it reaches equilibrium further increase in dosage does not have a significant effect.

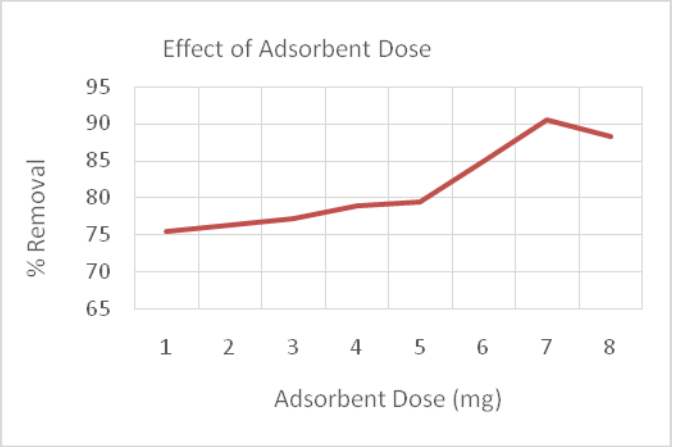


Fig 9- Effect of adsorbent dose

3.5 Effect of Temperature Variation

It was observed that an optimum temperature of 40°C was required for maximum adsorption.

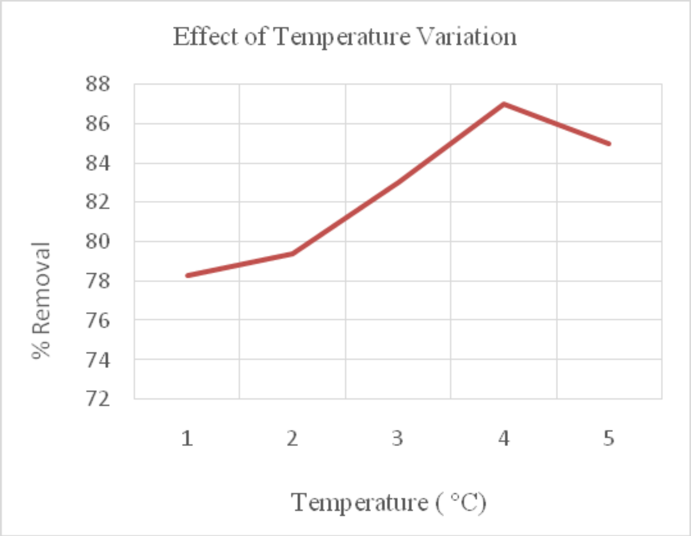


Fig 10- Effect of Temperature

3.6 Effect of Contact Time

The results show that adsorption capacity increases with increased time and attains equilibrium in 150 min as 91.16%.It was observed that in a period of 4 hours initially there is rapid increase in the % removal of metal ions in the first hour but once equilibrium is achieved the increase in contact time had no effect on removal efficiency which may be due to saturation of the adsorbent bed with the metal ions followed by adsorption- desorption process that occurs after saturation as shown in figure 11.

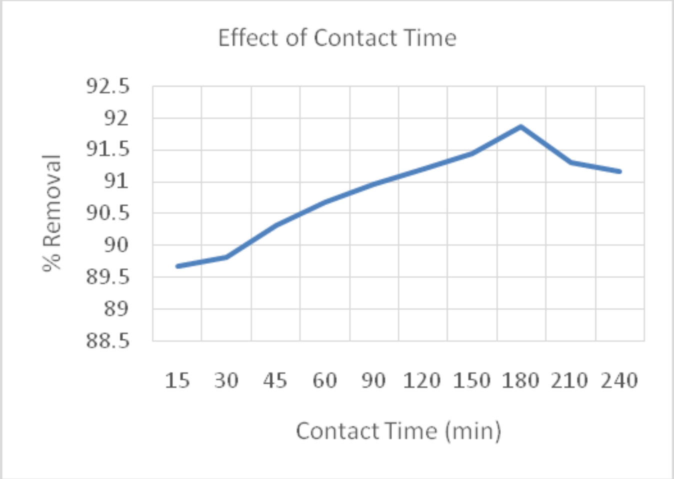


Fig 11- Effect of Contact time

3.7 Effect of pH Variation

The maximum adsorption of Cr (VI) ions was observed at pH 4.0 and significantly decreased by increasing the pH. At lower pH the surface of the adsorbent exhibits an increasing positive charge due to increasing H^+ since the species to be adsorbed i.e., Cr ions is also positive it experiences a repulsive force and thus adsorption is not favored and furtherH^+would also compete with Cr for the adsorption sites available thus reducing the uptake of metal ions by the adsorbent. On the contrary, as pH increases till pH 4, the adsorbent surface becomes negatively charged and favors the adsorption of positively charged metal ions increase. However, on further increasing the pH it results in precipitation of metal ions as its hydroxide.

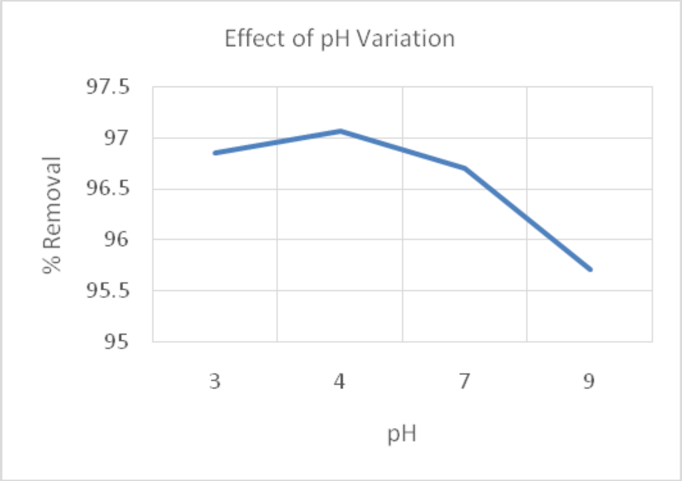


Fig 12- Effect of pH

3.8 Effect of Agitation speed

It was found that adsorption increases with an increase in speed of agitation. The maximum adsorption was found at 1000 rpm.On increasing the speed further the adsorption would decrease as the diffusion coefficient of metal ions will significantly get affected as the energy due to high speed probably would assist in breaking bonds formed between metal ion and their adsorbent. At lower speed of 200 rpm the degree of mixing reduces the process of adsorption.

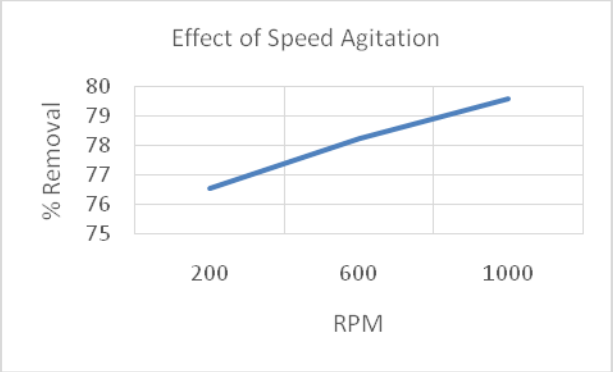


Fig 12- Effect of Agitation Speed

IV. CONCLUSION

This study shows that Cr (VI) can be removed by adsorption on silica alumina monoliths.Values of correlation coefficient for Langmuir isotherms is 0.9282 whereas for Freundlich, Temkin and Dubunin-Radushkevich the values are 0.8575, 0.6736 and 0.8379 respectively. It clearly indicates that Langmuir isotherm model validates for adsorption equilibrium studies.The Kinetic experiments show that the maximum adsorption of Cr (VI) was obtained at pH 4.0, adsorbent dosage of 7 g, contact time 150 min and temperature at 40°C.

ACKNOWLEDGEMENT

The authors would like to thank BCUD (Board of College and University Development), SPPU, Pune for funding the project.

REFERENCES

[1] S. A. Katz and H. Salem J. The toxicology of chromium with respect to its chemical speciation: a review Appl. Toxicol. 13, 1993, 217.

[2] Coulson, & Richardson's. (Manual of Chemical Engineering. Butterworth-Heinemann Publications 2002).

[3] Ali S., & Khalid, A. The removal of Zinc, Chromium, Nickel from industrial wastewater using corn cobs. Journal of Environmental Management, 55, 2A, 2014, pp 411-418.

[4] K.K. Singh, R. Rastogi, S.H. Hasan. Removal of Cr(VI) from wastewater using rice bran. J. Colloid Interf. Sci., 290, 2005, 61–68.

[5] M.Kobya, E. Demirbas, E. Senturk, M. Ince. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Bioresour. Technol., 96, 2000, 1518–1521.

[6] Doss V.R, Kodolikar S.P. A comparative study of 8-hydroxyquinoline-5-sulphonic acid and its 7-nitro derivative loaded on F-400 granular activated carbon for removal of copper ions from aqueous solutions. International Journal of Environmental Science.3, 6, 2013, 2049-2067.

[7] Dermentzis, K., & Christoforidis, A. Removal of Nickel, Copper, Zinc and Chromium from synthetic and industrial waste water by electrocoagulation. International Journal of Environmental Science.1, 5, 2011, 697-710.

[8] Dikshit, V., Agarwal, I. C., Shukla, P. N., & Gupta, V. K. Application of low-cost adsorbent for dye removal. Journal of Environmental Management, 90, 8, 2006, pp 2313-42.

[9] Amuda, O. S., & Ibrahim, A. O. Industrial waste water treatment using natural material as adsorbent. African Journal of Biotechnology. 5, 16, 2006, 1483-1487.

[10] Garg, U. K., Kaur, M. P., Sud, D., & Garg, V. K. Removal of hexavalent chromium from aqueous solution by adsorption treated sugarcane bagasse using response surface methodological approach. Journal of Hazardous Material. 171, 2009, 83-92.

[11] Idrish, S., Ndamistol, M. M., &Ebrahim, M. B. Adsorption Kinetics for the removal of biochemical oxygen demand (BOD) from dye effluent on to poultry dropping activated carbon. British Journal of Applied Science & Technology, 3, 3, 2013, 626-627.

[12] Manyuchi, M. M. Distillery effluent treatment using membrane bioreactor technology. International Journal of Scientific Engineering & Technology, 2, 12, 2013, 1252-1254.

[13] Rakholiya, V. V., & Puranik, A. S. Cod reduction using modifying industrial effluent treatment flowsheet and low cost adsorbent as a part of cleaner production. Advanced In Applied Science Research, 3, 3, 2012, 1279-1291.

[14] Rane, N. M., Sapkal, D. R., & Patil, M. B. Use of naturally available low cost adsorbents for removal of Cr (VI) from waste water. International Journal of Chemical Science & Application, 1, 2, 2010, 65-69.

[15] Safari, G. H. Post-treatment of secondary wastewater treatment plant effluent using a two stage fluidized bed bioreactor system. Journal of Environmental Science &Engineering, 11, 10, 2013, 56-64.

[16] Verma, S. K., Khandegar, V., & Saroha, A. K. Removal of chromium from electroplating industry effluent using electrocoagulation. American Society of Civil Engineers, 17, 2, 2013, 146-152.

[17] Safty, A. E., &Khairy, M. Optical detection/collection of toxic Cd (II) ions using cubic I and aluminosilica mesocage sensors. National Institute for MaterialsScience. 30, 98, 2012, 69-78.

[18] Nema T, Chan ECY, Ho PC. “Application of silica-based monolith as solid phase extraction cartridge for extracting polar compounds from urine”. Talanta. 82, 2010, 488-494.

[19] H. Minakuchi, K. Nakanishi, N. Soga, N. Ishizuka and N. Tanaka, “Effect of domain size on the performance of octadecyl silylated continuous porous silica columns in reversed-phase liquid chromatography”, Journal of Chromatography A, , 797, 1998, 121-131.

[20] P. D. Fletcher, S. J. Haswell, P. He, S. M. Kelly and A. Mansfield “Permeability of silica monoliths containing micro-and nano-pores”, Journal of Porous Materials, 18, 2011, 501-508.

[21] E. Alzahrani and K. Welham, “Design and evaluation of synthetic silica-based monolithic materials in shrinkable tube for efficient protein extraction”, Analyst, 136, 2011, 4321-4327.

[22] A. Galarneau, J. Iapichella, K. Bonhomme, F. Di Renzo, P. Kooyman, O. Terasaki and F. Fajula, “Controlling the morphology of mesostructured silicas by pseudomorphic transformation: a route towards applications”, Advanced Functional Materials, 16, 2006, 1657-1667.

[23] J. N. Kondo and K. Domen, “Crystallization of mesoporous metal oxides”, Chemistry of Materials, 20, 2007, 835-847.