STUDIES ON THE REMOVAL OF HEXAVALENT CHROMIUM CONTENT AT THE EXIT POINT OF RIVER GANGA AT KANPUR CITY USING   A SUITABLE ADSORBENT

Rita Awasthi & Deepti Shikha

Department of Chemistry, Brahmanand P.G. College, Kanpur, Uttar Pradesh, India.

ABSTRACT

The tannery industry mushrooming in North India has converted the Ganga River into a dumping ground. The tanning industry discharges different types of waste into the environment, primarily in the form of liquid effluents containing organic matters, chromium, sulphide ammonium and other salts. As per an estimate, about 80-90% of the tanneries use chromium as a tanning agent. Of this, the hides take up only 50-70%, while the rest is discharged as effluent. Pollution becomes acute when tanneries are concentrated in clusters in small area like Kanpur.

Removal of chromium ions from aqueous solution has been investigated under different conditions using a suitable adsorbent, i.e. activated charcoal. The experiments were conducted to study the effects of adsorbent dose, contact time, pH and temperature. The results showed that maximum adsorption of Cr(VI) was found at 40^0C and pH 2. Freundlich and Langmuir adsorption isotherms were also applied and they showed good fits to the experimental data.

Key words: Activated charcoal, adsorption, hexavalent chromium, temperature, River Ganga, pH.

1. INTRODUCTION

The major components of the tannery effluents are the toxic trace metals (Khwaja, 2001). Several analyses reveal high concentrations of chromium even in supposedly treated effluents. The majority of chemicals discharged into aquatic system eventually end up in sediments that may act as a sink of pollution as well as a source of pollution. Sediments are ecologically important components of the aquatic habitat which play a significant role in maintaining the trophic status of any water body (Singh, 1997). As reported earlier (Singh, 2002)**3)**, that highly polluted sediments are adversely affecting the ecological functioning of rivers due to heavy metal mobilization from urban areas into biosphere. Distribution of heavy metals in sediments of the river Ganga and its tributaries have been carried out by several workers (Ajmal, 1983; Subramania, 1987; Saikia, 1988; Jha, 1990; Ansari, 2000; Datta, 1998; Ramesh, 2000; Singh, 2001). Monitoring of Ganga River from Rishikesh to Varanasi indicated that Kannauj to Kanpur

and Varanasi are the most polluted stretches of the river Ganga (Singh, 2003; Tare, 2003). Analysis of upstream and down stream water and sediment revealed a 10-fold increase in chromium level in the sediment at the exit point of river ganga (Jajmau area) of Kanpur showing unchecked release of untreated tannery effluent (Khwaja, 2001).

Chromium (Cr) is a naturally occurring element found in rocks, animals and plants. It is present in different forms but the common forms are Cr(VI) and Cr(III).Out of which Cr(VI) which is more toxic. Cr(III) is essential for breaking down sugar, fat, protein inside an animal's body, thus making it vital for good health. In contrast hexavalent Cr can be detrimentally to health if exposed over a long period of time it may cause more bleed, ulcers, kidney and liver damage, cancer and even death. Excess amount of chromium uptake is very dangerous to us due to its carcinogenic effect. Chromium in soils affect plants growth (Shanber, 2003) it is non essential for micro organism and other life forms and when in excess amount, it exerts toxic effect on them after cellular uptake.Leather and chromium plating industries are the major causes for environmental influx of chromium (Baber, 1994; Barnhart, 1997). The movement of chromium & its bioavailability poses a potential threat to the environment. Cleaning up of the chromium contaminated sites is a challenging task because removal of Cr(VI) in aqueous solution is very difficult.

*Corresponding Author:

Rita Awasthi

Department of Chemistry, Brahmanand P.G. College, Kanpur, Uttar Pradesh, India.

Hence, proper treatment of tannery waste water is essential before releasing into the recipient environment. There are a number of methods employed (Boddu, 2003; Dupont, 2003; Dinesh, 2003; Gupta, 2001; Saumyen, 2005) for removal of hexavalent chromium from industrial waste water using various type of adsorbents, but in the present work activated charcoal has been taken as an adsorbent to remove chromium present in the river Ganga at Kanpur city.

2. EXPERIMENTAL

Material

Granular activated charcoal (S.D Fine chemicals, Mumbai, India) were used as such without further grinding and sieving. The properties of granular activated charcoal used for removal of chromium are listed in Table 1.

Table 1: Characteristics of activated charcoal.

Properties	Quantitative value
Moisture content	4.9%
Ash content	4.0%
Particle density	850 kg/m^3
Bulk density	500 kg/m^3
pH	5.3
Particle size	8-21 mesh

All the experiments were conducted is a 250 ml conical flask containing 100 ml of Cr (VI) containing water sample. After a definite interval of time the samples were withdrawn and filtered through Whatman No. 1 filter paper. The filtrates were analyzed for residual hexavalent chromium concentration by reacting it with 1,5 diphenylcarbazide. The absorbance measurement of the filtrate was also done by UV visible spectrophotometer (ELICO-SL-150) at 540 nm.

3. RESULTS & DISCUSSION

Effect of adsorbent dose and contact time

To study the influence of adsorbent dose and contact time for the removal of hexavalent chromium from water, sample the adsorption studies were carried out with different adsorbent doses at different interval of time (15 to 180 mins).

The adsorption of Cr(VI) increased with the increase in dose of activated charcoal. This may be attributed to the increased surface area and more available binding sites for adsorption on increasing the adsorption dose.

The removal of Cr(VI) by activated charcoal with various doses of 0.1 to 5.0 g/100 ml ranged from 65% to 96% and the equilibrium time was 120 minutes and after that percentage of removal was almost constant.

Effect of temperature

To investigate the effect of temperature on the adsorption of hexavalent chromium with the adsorbent dose of 1g/100ml was studied at 25^{0}C, 30^{0}C, 40^{0}C and 50^{0}C. It was found that maximum adsorption was found at 40^{0}C and then a decrease in adsorption was observed. This can be attributed to the fact that at lower temperature the kinetic energy of dichromate anions is low and so the contact between dichromate ions and active sites of activated charcoal is insufficient as a result adsorption efficiency decreases.. At higher temperature the kinetic energy of dichromate anion is higher than the attraction potential between the dichromate ions and active sites of activated charcoal. This conduction causes a decrease in adsorption efficiency (Daneshvar, 2002) which shows adsorption is more a physical property rather than a chemical property.

Effect of pH

The influence of pH solution was measured by studying the adsorption of Cr(VI) with adsorbent doses of 1g/100 ml of activated charcoal over a pH range of 2 to 10 as given in Table 2. The pH adjustment was made either by 0.1 N NaOH or 0.1 N HCl

Table 2: Effect of pH on percent removal of Cr(VI) by activated charcoal.

pH	Percent Removal of Cr(VI)
2	98
4	92
6	80
8	78
10	77.9

It is found that maximum adsorption by activated charcoal is noticed at pH 2 i.e. 98% followed by 92% at pH 4. The pH dependence of metal adsorption can largely be related to the ionic state of the functional group present in the adsorbent and also it can be related to the metal chemistry in the solution (Gupta, 2001). At low pH, the high adsorption of Cr (VI) can be explained by species of the Cr and the adsorption surface. At acidic pH, the predominant species of Cr are $Cr_2O_7^{2-}$, $Cr_3O_{10}^{2-}$ etc

(Raji, 1998) and at pH above 8 only $Cr_2O_7^{2-}$ is stable and as the pH decreases into the region 3-6, the equilibrium shifts to dichromate according to the overall equilibrium.

$$2\ CrO_4^{2-} + 2H^+ \longrightarrow Cr_2O_7^{2-} + H_2O$$
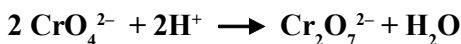
At much lower pH values, $Cr_3O_{10}^{2-}$ and $Cr_4O_{13}^{2-}$ species are formed. Thus decreasing pH results in the formation of polymerized chromium oxide species. In acidic conditions, the adsorbent's surface becomes highly protonated and favours the uptake of Cr (VI) in anionic form. As the pH increases, the degree of protonation of the surface decreases and so the adsorption decreases (Selvi, 2001). As the pH increases preference adsorption of OH^- takes place as compared to chromate ions as OH^- being a dominant species at higher pH values. The net positive surface potential of sorbent decreases and so adsorption capacity decreases.

Adsorption Isotherm

The distribution of Cr(VI) between the liquid phase and the solid adsorbent phase is a measure of the position of equilibrium in the adsorption process can be expressed by isotherm models. The data was fitted to Freundlich and Langmuir equations in linear form.

$$\log(q) = \log(k) + \frac{1}{n}\ \log C_e$$

Where q = amount of solute adsorbed per unit weight (mg/g) of the adsorbent used.

C_e = equilibrium solute concentration in the solution (mg/L)

k = Constants representing the adsorption capacity (mg/g).

n = constant representing the intensity of adsorbent

The values of constants k and n were obtained from the slope and intercept of a plot of log(q) versus log C_e. Both the parameters k and $\frac{1}{n}$ affect the adsorption isotherm. The higher the value of k and $\frac{1}{n}$ higher is the adsorption capacity. The Langmuir equation was applied to quantify adsorption capacity and is given below:

$$\frac{C_e}{q} = \frac{1}{bq_m} + \frac{C_e}{q_m}$$

Where, C_e = equilibrium solute concentration in the solution (mg/L)

q = equilibrium adsorption capacity

q_m & b= obtained from slope and intercept of a plot of C_e versus C_e/q .

It has been noted that larger the value of constant b, higher is the adsorption energy. Various experimental values and calculated values are shown in Fig.3 obtained from Freundlich and Langmuir isotherm and it yield R^2 value of 0.8937 for activated charcoal.

4. CONCLUSION

The adsorption of hexavalent chromium by activated charcoal in waste water is strongly dependent on pH, adsorbent dose, contact time and temperature. It can be concluded that the rate of Cr (VI) binding with adsorbent was greater in the initial stages, then gradually decreased and remained almost constant after an optimum period. The adsorption of Cr(VI) by activated charcoal was dependent significantly on pH and temperature. The results obtained in this study showed good fits to Freundlich and Langmuir adsorption isotherm. Thus activated charcoal could be effectively used for removal of Cr(VI) from polluted water.
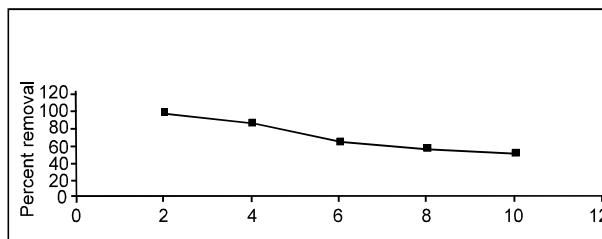

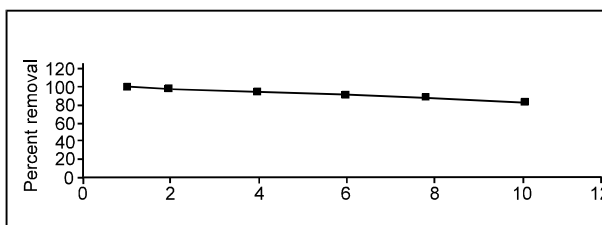Figure 1: Effect of pH on persent removal of Cr(VI) by AC

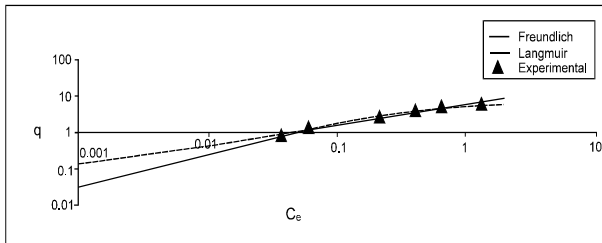Figure 2: Effect of initial concentration on persent removal of Cr(VI) by AC

Figure 3: Plot of experimental and calculated values from Freundlich and Langmuir isotherms for AC

REFERENCES

Ajmal M,. Khan MA, Nomani AA, Pollution in the river Ganges (India) Water Science and Technology, 1983, 16: 347-358.

Ansari AA, Singh IB, Tobschall HJ, Importance of geomorphology and sedimentation process for metal dispersion in sediments and soils of the Ganga plain: Identification of geochemical domains, Chem Geol, 2000, 162, 245-266.

Baber AJM, McGrath SP, Sidoli CMD, Reeves Res Cons Recy 1994, 11, 41-49.

Barnhart, Reg, Toxicol Pharma, 1997, 26, 53-57.

Boddu VM, Krishnaiah A, Jonathan LT, Smith ED, Environmental Science and Technology, 2003, 37, 4449-4456.

Daneshvar N, Salari D, Aber S, Journal of Harzard Materials, 2002, B 94, 49-61.

Datta DK, Subramanian V, Distribution and fraction of heavy metals in the surface sediments of the Ganges-Brahmaputra-Meghana river system in the Bengal besin. Environmental Geology, 1998, 36, 93-101.

Dinesh M, Kunwar PS, Vinod KS, Industrial and Engineering Chemical Research, 2003, 44, 1027-1042.

Dupont L, Guillon E, Environmental Science and Technology, 2003, 37, 4235-4241.

Gupta VK. Gupta M, Sharma S, Water Research, 2001, 35, 1125-11.

Gupta VK, Srivastava AK, Jain N, Water Research, 2001, 35(17), 4079 – 4085.

Jha PK, Subramanian V, Sitasawad R, Van Grieken R, Heavy metals in water and sediments of the Yamuna river (a tributary of the Ganga), Science of the Total Environment, 1990, 95: 7-27.

Khwaja AR, Singh R, Tandon SN, Monitoring of Ganga water and sediments vis-a-vis tannery pollution at Kanpur (India): A case study, Environmental Monitoring and Assessment, 2001, 68 (1), 19-35.

Ramesh R, Ramanathan AL, Ramesh S, Purvaja R, Subramanian V, Distribution of rare earth elements in the surficial sediments of the Himalaya river system, Geochemical Journal, 2000, 34: 295-319.

Raji C, Anirudhan TS, Water Research, 1998, 32(12), 3772-378.

Saumyen G, Riya B, Water Environment Federation, 2005, 77 (4), 411-41.

Selvi K, Pattabhi S, Kadirvelu K, Bioresource Technology, 2001, 80, 87-89.

Shanber A, Djanaguiraman M, Pathmanabhan G, In proceedings of the International Conference on water and environment (WE 2003) India, P. 9-13 (2003).

Saikia DK, Mathur RP, Srivastava SK, Heavy metals in water and sediments of upper Ganga, Indian Journal of Environmental Health, 1988, 31(1), 11-17.

Singh M, Ansari AA, Muller G, Singh IB, Heavy metals in freshly deposited sediments of Gomti river (a tributary of the Ganga river): Effects of human activities, Environmental Geology, 1997, 29 (3/4): 246-252.

Singh M, Muller G, Singh IB, Heavy metals in freshly deposited stream sediments of rivers associated with Urbanization of the Ganga plain, India, Water Air and Soil Pollution, 2002, 141, 35-54.

Singh M, Heavy metal pollution in freshly deposited sediments of the Yamuna river (the Ganga river tributary): A case study from Delhi and Agra urban centres, India Environmental Geology, 2001, 40, 664-671.

Singh M, Muller G, Singh IB, Geogenic distribution and baseline concentration of heavy metals in sediments of the Ganges River. India, Journal of Geochemical Exploration, 2003, 80, 1-17.

Subramania, V, Van Grieken R, Vant Dack L, Heavy metal distribution in the sediments of Ganga and Brahmaputra Rivers, Environmental Geology and Water Sciences, 1987, 9, 93-103.

Tare V, Yadav AVS, Bose P, Analysis of photosynthetic activity in the most polluted strech of river Ganga, Water Research, 2003, 37: 67-77.