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Removal of Chromium From Groundwater using Neem Leaves as Adsorbent

Elangovan, N.S.*, Lavanya, V. and Arunthathi, S.

Department of Civil Engineering, Jerusalem College of Engineering, Chennai – 600100, Tamil Nadu, India

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ABSTRACT: The effluents of tannery industries are the major source of chromium contamination in the groundwater. In most of the sub-urban areas ground water is the major source of drinking water. For human being Long term exposure to chromium is detrimental. The main objective of this study is to assess the groundwater contamination and to adopt appropriate methods and to develop suitable techniques either to prevent chromium contamination or to reduce it to very low levels with due consideration to cost optimization. Bore well samples were collected from 6 location from the proximity of tannery industry at a distance of 25m interval and at different depth during 2014 in the month of March. To remove the chromium from the groundwater neem leaves is used as the adsorbent. The column study was conducted to determine the effect of adsorbent to remove the chromium concentration from the ground water. To investigate the influences of bed height on the performance of chromium adsorption on to the neem leaves in a fixed-bed column. The results reveal that the concentration of chromium is high near the tannery industry in Chrompet so the study concluded that usage of groundwater in Chrompet should be avoided.

Key words: Groundwater, Contamination, Chromium removal, Adsorbtion, Neem leaves

INTRODUCTION

Chromium is one of the most abundant metal present in the earth crust. Chromium is an odorless and tasteless metallic element. Chromium is found naturally in rocks, plants, soil and volcanic dust, humans and animals. The most common forms of chromium that occur in natural waters in the environment are trivalent chromium (chromium-III), and hexavalent chromium (chromium-VI). Both valences of chromium are potentially harmful being mutagen and also carcinogen (Altundogan 2005; Dakiky *et al*., 2002).The extensive use of chromium in leather tanning, metallurgy, electroplating and other industries has resulted in the release of aqueous chromium to the groundwater at various sites; especially tannery industries are causing high chromium contamination to the subsurface. In India 1200 tannery industries were using chrome for tanning the leather and discharging the waste water without proper treatment this may be the major reason for persistence of chromium in the ground water (Brinda *et al*., 2010) The presence of chrome in waters destined for potable drinking use have the potential to cause damage to liver, kidney, circulatory and nerve tissues and skin irritation from long-term exposures at levels above the Maximum Contaminant Level (MCL). Currently, the US Environmental Protection Agency's (EPA) MCL in drinking water for chrome has been set at 0.1 parts per million (ppm).

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

Conventional methods for removing Cr (VI) ions from industrial wastewater include reduction (Kim *et al.*,2002), reduction followed by chemical precipitation (Ozer *et al.*, 1997), adsorption on activated carbon (Lotfi and Adhoum, 2002),These methods have found limited application because it is not economically justifiable and generate chemical sludge which forms secondary pollutant and its disposal becomes an issue. Adsorption is an effective and adaptable method due to its simple design, less operative cost and ease operation. Therefore the research interest has been increased in using alternative low –cost adsorbent and identifying various influencing factors includes adsorbent bed height, hydraulic loading rate (Datta *et al*., 2013). Natural materials that are available in large quantities or certain waste products from industrial or agricultural operations may have possible as low-cost sorbents (Ahalya *et al*., 2010). The removal of chromium from ground water is simply an adsorption process and does not involve any chemical reactions. Leaves or carbonaceous product on burning gets activated; the activation is simply the process of increasing the surface area of the carbon atom and inducing a positively charged atom. The charged atom owing to its increased surface area readily adsorbs negative ions, removing taste, odour and finally purifying the water for drinking and domestic purpose. In recent years, Some of the researchers have used both natural and synthetic material as adsorbent for removal of heavy metals and few authors used chemically treated natural materials as adsorbent for removal of heavy metals from the aqueous solution. Some of the adsorptive material such as green algae (Malkoc *et al*. 2003, Gupta *et al*. 2001) , maple sawdust (Yu *et al*. 2003), a sugar industry waste (Gupta & Ali 2004a), oriental beech sawdust (Acar & Malkoc 2004), distillery sludge , soya cake (Daneshvar *et al*. 2002), persimmon tannin gel (Nakajima & Baba 2004), duolite (Gupta *et al*. 2004b), bagasse fly ash (Gupta *et al*. 2003), red mud (Gupta & Sharma 2002), activated carbon derived from fertilizer waste (Mohan *et al*. 2001), activated rubber wood sawdust (Kalavathy *et al*. 2005), tea factory waste (Malkoc & Nuhoglu 2005, Cay *et al*. 2004) granular ferric hydroxide (Mukhopadyay *et al*. 2007) has used in heavy metal removal from wastewaters and drinking water in meeting standards.

Among all the natural adsorbent Azadirachta Indica (neem) leaves has high potential to remove the heavy metals. In India, Azadirachta Indica is a tree which is commonly seen is southern part of India, the leaves of this tree is burnt and the burnt carbon can be utilized for the purification of water at a cheaper cost without heavy operation. Cr (VI) has been removed by neem leaves powder (Tawde and Bhalerao, 2010). Some of the study reports the biosorption kinetics and the biosorption equilibrium of Zinc by Neem leaves and stem bark powder (Arshad, *et al* 2008). Neem bark powder (NBP) has also been used as an adsorbent for the removal of hexavalent chromium from aqueous solutions (Saravanakumar and Phanikumar 2012). The potentiality of Neem has been widely studied by different researchers for solving various problems related to agriculture, public health, population control and environmental pollution (Arshad, *et al* 2008). Hence in the present work, Azadirachta indica (Neem) leaf powder is studied for their adsorptive capacity to remove chromium (VI) from aqueous solution. The study focused on the contaminant transportation to different layer of subsurface area.

Fig. 1. Final Adsorbent

MATERIALS & METHODS

Chromepet is the hometown for the small and large scale tanning industries. This area is sub urban area located in the Chennai city. Chrome–Tanning is the popular method practiced in this area and hence it is named as Chromepet. It is situated in the out skirts of Chennai city in Tamil Nadu. The study area is 13km away from the Bay of Bengal. The climate of this area is with high temperature and low humidity. During winter the temperature was around 20°c and maximum of 44°c during summer. There are totally 147 small and large scale tanning industries situated in the Chromepet, these industries are the completely responsible for the groundwater pollution in the Chromepet. Most of the lower socio economic community depends on groundwater for their domestic purposes. Hence it is essential to identify the cost effective natural material to treat the groundwater in the domestic domain itself. The study collected the 6 bore well samples from the proximity of tannery industry at a distance of 25m interval and at different depth during 2014 in the month of March as shown in Fig. 2 to evaluate the migration of chromium into the groundwater from a tannery effluent. The samples were collected in clean white 1 litre capacity leak proof container. Before sample collection, the container was rinsed with the water to be sampled three times. The

Table 1. Equipments and Methods of physico- chemical parameter

S.NO	Parameters	Instruments
1	Color	Cobalt scale
2	pH	pH electrode
3	Turbidity	Nephelometric turbidity meter
4	Total suspended solids & dissolved solid	Evaporation method
5	Chromium	ICPMS/OPES

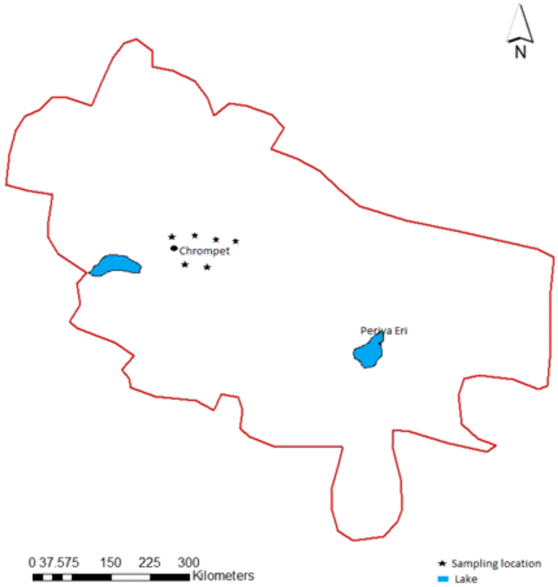

Fig. 2. Study area with sampling location

physical parameters considered for the study include color, pH, Total Dissolved Solids (TDS), Total suspended solids (SS) The physico-chemical analysis of the groundwater samples was performed at Jerusalem college of engineering, environmental engineering laboratory. The analyses were based on the standard methods prescribed by the American Public Health Association (APHA 1998). The methods used for the physico-chemical and heavy metal analyses are given in Table 1.

To determine the ability of neem leaves to remove the chromium from aqueous solution and to investigate the influences of bed height on the performance of chromium adsorption on to the neem leaves in a fixed-bed column the study used Activated carbon extraction of Azadirachta Indica leaves as adsrbent to reduce the concentration of chromium in groundwater. According to the recommendation of The World Health Organization (WHO), the maximum allowable limit for total chromium in drinking water is at the level of 0.00005 g/L. Initially neem leaves were washed repeatedly by using distilled water to remove moisture and soluble impurities. Then neem leaves kept in dryer at 90 ºC, for 2- 3 hours till leaves turn pale yellow. Then crushed and screen by 10-15µm mesh size. Neem leaves powder washed to remove moisture and free acid and kept in dryer 20-25 minute. After drying powder was mixed with ortho-H_3PO_4 (Phosphoric acid) in silica crucible and kept in furnace at 260^0c for 15-20 minute.

The heating period depend on atmospheric temperature then solution was cooled & repeatedly washed using hot water to remove free acid and moisture, total 7 washing taken and kept it in dryer for 20-25 minute the prepared black colored adsorbent kept in bottle for further use. About 20 gm of sample and 10ml Ortho-H_3PO_4 acid taken in silica crucible and kept in furnace. The furnace is initially at normal room temperature then furnace set at 260^0C. Heating was carried out for 20 minute. Then sample was removed and cool. After cooling the sample was repeatedly washed for 7 times using hot water to remove free acid and moisture .Then sample kept in dryer for 20-25 minute and the activated black colored adsorbent stored in bottle as shown in Fig. 1.

The experimental column made up of borosilicate glass of 30 mm diameter with varying depth of adsorbent. After measuring the weight previously activated neem leaves is packed up to a bed height in the column. Columns are mounted vertically and glass wool used at the bottom of the column acts as supporting material of the adsorbent bed and also serves the purpose of filtration of the adsorbent particles. Control valves after the overhead tank helps to regulate the flow and a graduated burette to measure the influent liquid flow rate are incorporated in the feed line of the column. After maintaining the flow rate of 1.5 ml/min. All the experiments carried out at the room temperature 30° C ± 4° C . The residual concentration of chromium in aqueous sample was determined using inductively coupled plasma/Optical emission spectrometry.

To determine the optimum depth for a standard quantity of water say 250ml water sample, bed depth ranging from 15cm to lower value i.e., 15cm, 12cm, 9cm, 6cm, and 3cm is setup in the column at a flow rate of 1.5 ml/min. The dosage of adsorbent containing initial concentration of 10 mg for 3cm depth of bed 20, 30,40,50mg for 6cm 9cm,12cm and 15cm respectively. The depth at which the extent of chromium removal begins to change is the critical depth and the optimum depth for the given sample will be slightly higher than this depth. The percentage removal of chromium is calculated as

$$\% \text{ Removal} = Co\text{-}Ct \times 100/Co$$

Where, Co: Initial Chromium concentration

Ct: Chromium concentration at equilibrium after treatment with adsorbent

RESULTS & DISCUSSION

The Table 2 illustrates that the high concentration of chromium was observed in the bore well which is situated at 150m distance from tannery. Similarly decreased concentration of chromium was observed in increased depth. The ground water table in the depth of 150 feet is severely affected by the effluents released

Table 2. Concentration of chromium and other physical and chemical parameters before treatment

Sample ID	distance from tannery (m)	bore well depth (feet)	color	Chromium mg/l	Odour	pH	Turbidity (NTU)	TSS (mg/l)	TDS mg/l
1.	150	130	13	0.1	4	9.3	57	970	6800
2.	175	145	10	0.08	3	9	50	940	6500
3.	190	150	7	0.07	3	8.7	45	890	6200
4.	220	300	6	BDL	3	8.5	20	800	6000
5.	250	320	6	BDL	3	8	20	800	6000
6.	260	330	6	BDL	3	8	20	700	6000

Note BDL - Below detectable limit

Table 3. Concentration of chromium and other physical and chemical parameters after treatment

Parameter	Adsorbent Depth With Removal Concentration				
	3 cm	6 cm	9 cm	12 cm	15 cm
Chromium	0.07	0.04	0.04	0.04	0.04
Colour	7	0	0	0	0
Odour	0	0	0	0	0
Turbidity(NTU)	15	0	0	0	0
pH	8	8.1	7.4	7.3	7.2
TSS(mg/l)	32	22	18	7	7
TDS(mg/l)	3600	1750	820	115	115

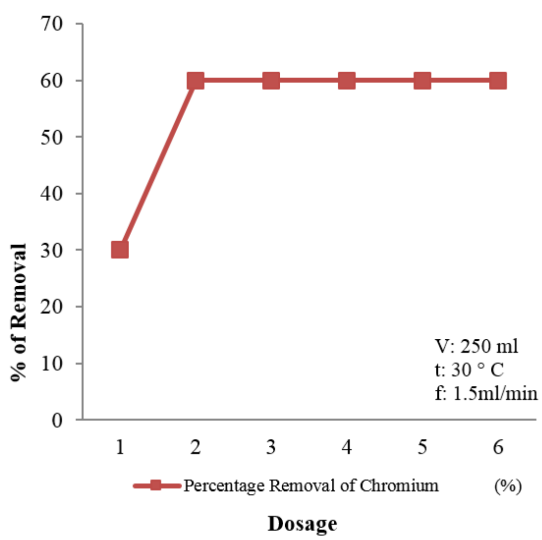

Fig. 3. Effect of Adsorbent dosage on the removal of chromium

by the tanning industries. Among 6 samples collected, first location which is very near to the tannery industry alone having greater chromium concentration, this sample alone taken for the study on chromium removal by column study. The physical and chemical parameters are greater than the permissible limit. The colour of the sample is 13 in cobalt scale which shows that water is completely unfit for the drinking purpose from the psychological point of view. Then the odour is a serious factor which is considered to be a main factor in drinking standards, the Threshold Number of 4 is completely undesirable. Turbidity is a not a serious factor whereas Nephelometric Turbidity Unit of 57 units shows that the water is highly turbid in nature. pH is the important factor in adsorption process as it influence the surface charge of adsorbent. The degree of adsorption increases when the sample is alkaline especially for neem leaves (T awde and Bhalerao, 2010). pH value of the sample analyzed shows that the water is slightly alkaline in nature. The total suspended and dissolved solids are also greater than the permissible limit. Even the figure looks quite dominative it can be reduced easily by treatment methods. The table 3 shows the concentration of chromium and other physical and chemical parameter after treatment with neem leaves. The experiments were carried out at constant flow rate of 1.5mL/min and with altering bed height ranging between 3cm to 15cm. The result of this experiment is shown in the Fig. 1 below. From the study it is seen that the concentration of the hexavalent chromium decreases with the increasing bed height. This fact can be explained by the phenomenon that with the increase of bed height the length of bed through which the influent passes also increases. The final concentration of Cr-VI in the water sample at the depth of adsorbent 3cm is 0.07ppm which is greater than the permissible limit as per IS-10500. At the adsorbent depth of 6cm the final concentration of chromium is 0.04ppm. At the 6cm depth of adsorbent the chromium concentration is slightly lesser than the permissible limit which is desirable for 9cm, 12cm and

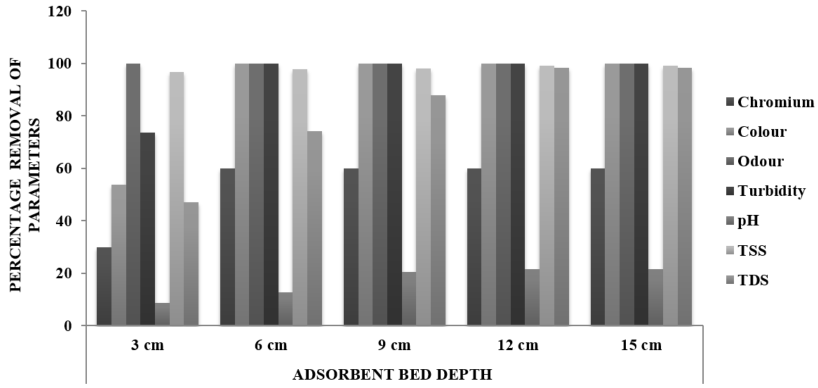

Fig. 4. Percentage Removal of Physical and chemical parameters

15cm the chromium concentration remains constant. From the concentration of all the above values for respective adsorbent depths the optimum value of adsorbent for the chromium removal is 6cm or slightly greater than this height. Colour is one of the important parameter for deciding the water is completely potable. The variation of colour with the depth of adsorbent is shown in table 3 The Odour analysis is done by threshold number. From the depth of 3 cm of adsorbent the odour is completely removed and the sample is completely odorless. The value remains constant till the adsorbent depth of 15cm. For the odour is concerned the optimum depth of adsorbent is determined as 3cm. Turbidity is mainly depends on the amount of suspended particles present in the water. The turbidity is determined by Nephelometric Turbidity Meter. The permissible limit of turbidity in drinking water as per IS-10500 is 5 to 10 NTU. The results of turbidity after the column study are shown in table 3. The efficiency of removal of suspended solids were upto 6cm depth of bed, The gradual decrement of Suspended solids and dissolved solids were observed up to the depth of 9cm. At 12cm and 15cm the constant concentration of solids is recorded. The optimum depth of adsorbent is determined by considering all the parameters. The adsorbent depth at which maximum removal is taken place can be determined as optimum depth. Effect of dosage of adsorbent on percentage removal chromium was determined by increasing the amount of adsorbent is shown in Fig 3 the % removal increased from 30% to 60% as the amount of neem powder was increased from 10 g/L to 20 g/L. The increase in percentage adsorption with increase in adsorbent dosage is due to the increase in the number of adsorption sites. (Sharma and Forster, 1993; Selvaraj *et al.*, 1997). As shown in Fig. 4 the amounts of removal efficiency of hexavalent chromium were minimum in 3cm depth of bed the reason may be contact time with adsorbent is less, but these efficiencies were considerably increased may be due to the contact time maximized at 6cm bed. According to Fig. 4 it could be concluded that the depth of 6cm bed of adsorbent is highly efficient in the reduction of all the parameters within the permissible limit., especially hexavalent chromium adsorption was enhanced by increase in adsorbent dosage, so this depth is taken as the optimum depth. The present study assessed the chromium contamination in the groundwater and developed an economical and effective adsorbent for the removal of chromium ions from aqueous solution. In the tannery effluent the chromium is persist as trivalent chromium which is less toxic, when it is discharged into the soil it gets oxidized into hexavalent chromium, which may lead to chronic diseases due to long term exposure (Anderson 1999, Govil *et al*,2004, Gowd *et al* 2005)**.** Chromium VI can be removed efficiently by using activated neem as adsorbent.

CONCLUSIONS

The usage of groundwater for domestic purposes in the Chrompet for a distance of 15m from tannery industry should be avoided, as the groundwater has high concentration of Hexavalent chromium. Neem leaves are the cost effective adsorbent to remove the chromium from the groundwater. Adsorption of Cr (VI) ions through activated neem leaves in 3cm bed depth was 30% and in the 6cm bed it has increased to 60% therefore neem is an economically effective natural adsorbent for removal of chromium from ground water.

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