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Batch Adsorption and Transport of Heavy Metal CR (VI) on Agriculture Soils

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ABSTRACT

Pollution is a problem all over the world because it has an impact on every part of the environment. Pollutants from human- or machine-made sources circulate endlessly throughout ecosystems, eventually reaching humans via the food chain. Industrialization combined with inadequate effluent disposal and management is largely to blame for the prevalence of toxic metals in Africa and other developing countries.

Major effluents from tailings, electroplating, include toxic metals like Cr (VI), Zinc (Zn), Lead (Pb), which contaminate surface and underground water, soil, and food and disrupt biological function and growth. Because of this, industrial wastewater effluent requires treatment.

Adsorption technique is one of the most technologies being used for treatment of water and waste water and the object of study is to select the low cost adsorbent. This work focus on the chromium (VI) adsorption from wastewater. Shows the effect of contact time, Dosage and pH on Cr (VI) removal and focuses on obtaining the breakthrough curves and retardation coefficients for various concentrations using naturally available adsorbents to find out the time at which the soil column bed gets exhausted.

Keywords "Adsorption, Chromium, Contact time, Dosage, pH."

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INTRODUCTION

The resources of earth are used every day by all living things except humans. To ensure his future as an individual, member of society, and citizen of his country, man makes use of and exploits all the earth's resources. Overpopulation and industrialization, driven by men's need to provide for their families now and in the future, are draining the planet dry of its natural resources. We are polluting our air, soil, and water due to our excessive use of natural resources.

Pollution is a problem all over the world because it has an impact on every part of the environment. Pollutants from human- or machine-made sources circulate endlessly throughout ecosystems, eventually reaching humans via the food chain. Poor effluent disposal and management add substantially to the prevalence of toxic metals in developing countries (Okereafor *et al.* 2020).

Major mining effluents from tailings, electroplating, and other industries include toxic metals like chromium (Cr), zinc (Zn), lead (Pb). which contaminate surface and groundwater, soil, and food. Pesticides, agrochemicals and toxic metals are the

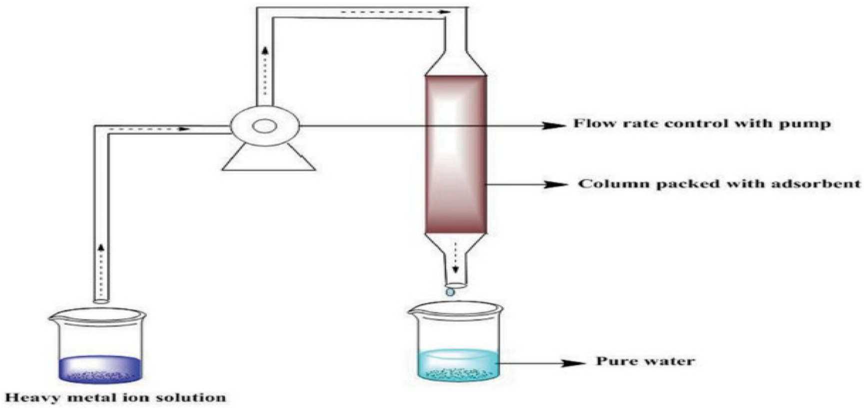

Fig. 1. Schematic diagram showing adsorption process by continuous column for heavy metal ions removal.

root causes of environmental toxicity in livestock.

Agricultural, pharmaceutical, atmospheric, industrial, domestic effluents and geogenic activities are all well-known sources of toxic metals in the environment (He *et al.* 2005). The mining, foundry, and smelting industries, along with other metal-based industrial operations are examples of "point source" industries that frequently degrade their surrounding environments (Arruti *et al.* 2010, Strater *et al.* 2010).

Although these toxic elements occur naturally within the earth's crust, environmental contamination and human exposure to them are caused by anthropogenic activities like mining, electroplating, smelting operations, domestic and agro-allied industries and geogenic activities (He *et al.* 2005).

Water is a vital component of life on earth. Water is essential for the survival of all forms of life. Without water, all forms of life (including plants, animals, humans and other organisms) will quickly perish.

Water pollution and fresh water scarcity are both exacerbated by the industrial wastewater streams that are discharged into the environment. Most of the water is not usable and its highly uneven spatial distribution makes it difficult to develop and manage water resources. Thus, water's significance has been acknowledged and efforts are being redirected toward more efficient and cost-effective management of this precious resource.

Heavy metals in industrial effluents are becoming an increasingly difficult problem for businesses to solve as government legislation becomes more stringent in most developed countries. Due to its low cost, sludge minimization, adsorbent regeneration, and metal recovery, adsorption is a potent method for heavy metal sequestration from effluents. Plant husk, pine needle, cactus leaf, neem leaf powder, rice brine, wheat brine, saw dust, moringa seed shells, mango seed shells, besharam stem powder, orange peel, maize cobs, peanut shells, soya bean hulls, water hyacinth pulp powder, jack fruit, coconut fiber pith, coconut shell fiber, plant bark and coconut fiber. Numerous applications exist for these types of agricultural discards (Renu Bisht *et al.* 2015).

Common sources of heavy metals in the environment include industrial wastewater discharges. The harmful effects of these heavy metals on the environment are of great concern. Heavy metals are not broken down by natural processes, so they accumulate in living things and trigger all sorts of diseases and disorders (Susane. Bailey *et al.*1998).

Metal toxicity

Toxic metals affect the majority of metabolic and physiological processes in all living organisms (Teresa *et al.* 1997). Some potentially toxic metals, such as Cu, Co, Zn, Ni and Cr, are both micronutrients and essential components in redox processes.

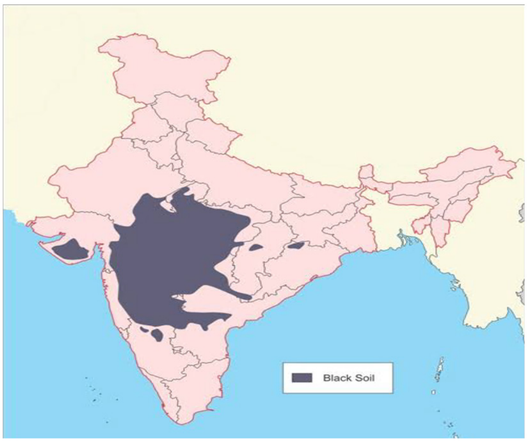

Fig. 2. Availability of black cotton soil.

Because metals can bio accumulate in food sources and endanger human and animal health Aycicek *et al.* (2008), Aschner *et al.* (2002), metal toxicity is a highly discussed topic in environmental health. The harmful effects of toxic trace metals (elements) depend on a number of factors, including the dietary concentration of the elements, the system's ability to absorb such elements, the body's ability to maintain homeostatic control of such elements, and the species of animal involved (Rajaganapathy *et al.* 2011).

Table 1. Physico-chemical properties of adsorbent.

Sl. No.	Characteristics	Units	Fuller's earth	Laterite soil	Black cotton soil
1	Moisture content	%	2.22	3.44	5.86
2	Decolorizing power	mL/g	13.5	18	21
3	pH values	- - -	7.8	7.6	7.1
4	Specific gravity	- - -	1.88	2.40	2.54
5	Surface area	m^2/g	750	453	520
6	Bulk density	g/cc	0.923	1.140	1.105
7	Color	- - -	Light gray	Red	Black

Potentially toxic metals in soil and their implications

Soil micronutrients and macronutrients are said to be Chemical Time Bombs (CTBs) (Wood *et al.*1974) based on the findings of several studies into soil contaminants from anthropogenic activities in various geographical locations. Both enzymatic and microbial activities (Chao *et al.* 2014, Lee *et al.*1996) are influenced by the soil's quality. Microbial biomass is an important indicator that could be used to measure the level of soil contamination (Aceves *et al.* 1999).

Furthermore, plant uptake of soil toxic metals is not always a problem in the short term but becomes a cause for concern in the long run. That's when the levels of these poisonous metals reach dangerous heights, killing plants because they can't process the toxins. Increased soil zinc levels reduce plant metabolism, leading to slower growth and premature ageing. When soils contain an abundance of toxic metals, human health takes a major hit. Ingesting contaminated food, water, and air, in addition to dermal absorption of toxic metals, contribute to this problem.

Potentially toxic metals in water and their implications

There has been a worldwide increase in the number of deaths caused by diseases associated with contaminated drinking water, including the deaths of farm animals and humans.

No environmental or enforcement group has been able to successfully curb the activities that produce these metals (WHO 1995). These unnecessary metals

Table 2. Optimum contact time, dosage and pH for Cr (VI) removal by naturally available adsorbents.

Parameters	Fuller's earth	Laterite soil	Black cotton soil
Optimum contact time (in minutes)	70	110	90
Optimum dosage (in mg)	800	1000	1200
Optimum pH	2.0	2.0	4.0

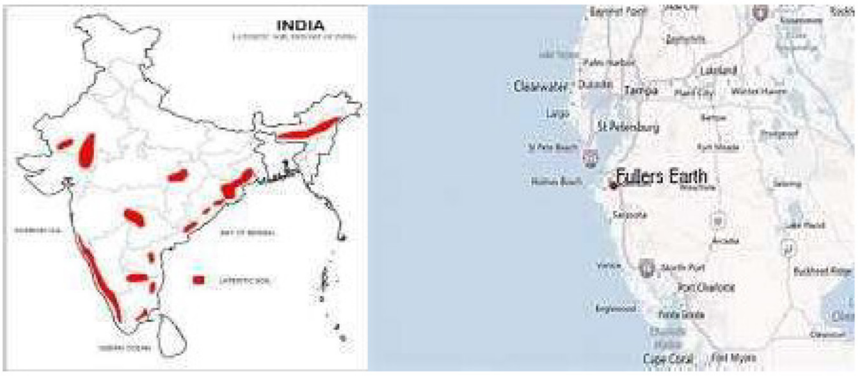

Fig 3. Availability of laterite soil and Fuller's earth.

have severely hampered most biological processes. The presence of toxic metals, which are toxic even at low concentrations, compromises the quality of water and has a negative effect on human, animal, and plant life.

Untreated sewage in the Musi River in Hyderabad, India, has been found to be severely contaminated with Cd, Ni, Pb, Co, Zn, and Cu, at mean concentrations of 0.025, 0.062, 0.210, 0.053, 0.003, and 0.011 ppm, respectively (Raj *et al.* 2006). These numbers were worrisome because they were well above the thresholds set by the World Health Organization.

Potentially toxic metals in plants and their implications

Excessive levels of toxic metals have been shown to stunt plant growth (Masindi *et al.* 2018), (Moustakas *et al.*1994). Research shows that the elements Mn, Pb, Cd, Cr, and Co are to blame for stunted development in maize (*Zea mays* L.) plants (Abdul *et al.* 2010). Plants may experience oxidative stress from exposure to toxic metals, cell structure mutilation from the toxic metals being substituted for deficient elements, and a slowing of photosynthetic processes in the plant if these metals are present in high enough concentrations (Van Assche *et al.*1990).

Adsorption

Adsorption is analogous to a cleaver, as it transfers the atoms of a fluid stage, such as a gas or fluid, to a solid surface. This results in a heterogeneous framework consisting of two or more liquid stages, one of which is the powerful adsorbent. Particles that have been adsorbed onto robust surfaces are called adsorbates,

Table 3. Data showing the up-flow values of freundlich coefficients on Cr (VI) adsorption.

Adsorbent	Concentration in mg/L	KF (Coefficient of freundlich isotherm)	1/n (coefficient of freundlich isotherm)	KFd (Distribution coefficient)	R (Retardation coefficient)
Fuller's earth		1.104	0.175	0.073	0.99
Laterite soil		1.092	0.159	0.075	0.98
Black cotton soil	10	1.148	0.216	0.069	0.96
Fuller's earth		1.104	0.175	0.045	1.08
Laterite soil		1.092	0.159	0.047	1.09
Black cotton soil	15	1.148	0.216	0.042	1.07
Fuller's earth	20	1.104	0.175	0.032	1.06
Laterite soil		1.092	0.159	0.033	1.06
Black cotton soil		1.148	0.216	0.030	1.05

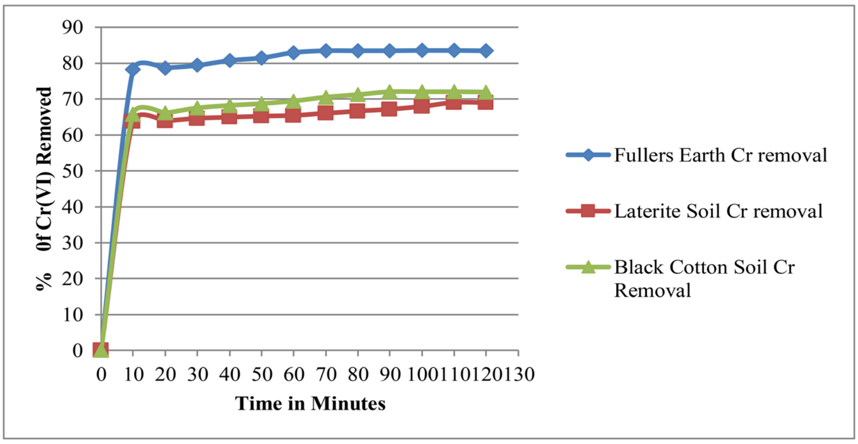

Fig. 4. Influence of contact time on Cr (VI) removal by red soil, black soil and fullers earth.

and the surfaces onto which the particles have been adsorbed are called the substrate or adsorbent. The interface, or transition zone, is where the adsorption process takes place.

Adsorption typically occurs on the walls of pores, making most adsorbents highly permeable materials. There are many situations where the components are held firmly enough to permit complete evacuation of a component with negligible adsorption of other components. There are three methods that can be used to accomplish adsorptive partitioning: steric impact, kinetic impact, and equilibrium separation.

The steric effect is determined by the atomic sieving property of zeolites. Success in Kinetic Separation is based on the underlying tenet that different molecules diffuse at different rates. Most processes rely on equilibrium adsorption to separate substances from solutions and these are known as equilibrium separation processes. In this report, we will concentrate on illustrating the procedure of equilibrium separation. Removal of heavy metal ions via adsorption using a continuous column is depicted in Fig.1 below (Chakraborty *et al.* 2020).

Types and mechanism of adsorption

Based on the bonding between the adsorbate molecules and the solid surface, adsorption can be cate-

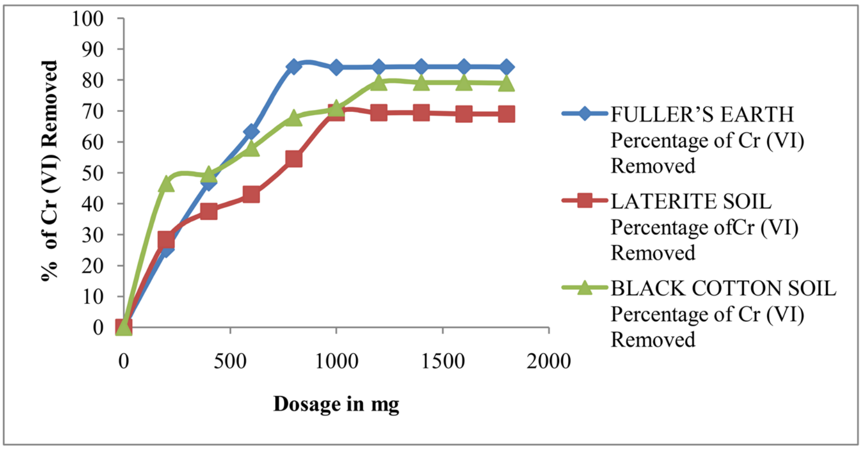

Fig. 5. Influence of dosage on Cr (VI) removal by red soil, black soil and fullers earth.

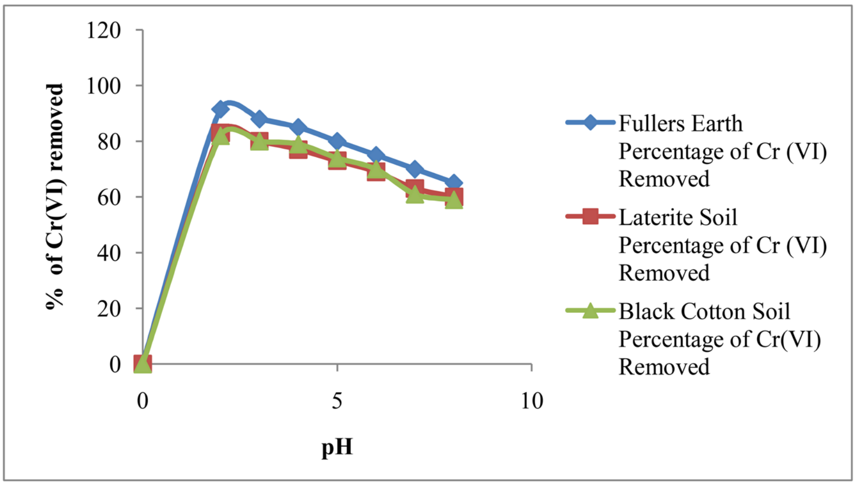

Fig. 6. Influence of pH on Cr (VI) removal by red soil, black soil and fullers earth.

gorized as :

Physical adsorption.
Chemical adsorption
Ion exchange adsorption

Physical adsorption typically occurs in a nonspecific manner due to the activation of the Vander Waals constraint of fascination. The strong surface does not restrict the movement of the adsorbed atom, which means that it is not confined to a single spot. There's also a chance that the fabric will condense on the adsorbent and stack up in a few layers. Most physical adsorption is reversible, meaning that the fabric is adsorbed to the same degree as the concentration drops. To put it another way, the forces responsible for chemical adsorption are on a much grander scale than those responsible for the arrangement of chemical compounds. Particles are confined to their surface locations because the adsorbed fabric forms a layer over the surface that is consistently one atom thick. When a monomolecular layer forms over the surface, the adsorbent's capacity is greatly reduced.

In addition, chemical adsorption is typically irreversible. Adsorbed substances can be released by heating the adsorbent to a higher temperature. Adsorption in which the adsorbates are attracted to the surface due to an electric charge is known as "exchange adsorption.

"Ion Exchange is covered in this seminar. Here, Electrostatic attraction causes particles of a substance to cluster at the surface; the stronger the attraction, the smaller the particles (in terms of hydrate radius) can be. There are important differences between the three types of adsorptions, but sometimes it's hard to put an adsorption into a single category. The sorbet solutes are prevented from redesorbing inside the setup by an adsorption process. Even out when the total number of solutes adsorbed and desorbed is the same. In this way, adsorption and desorption rates will balance out to a point where the system is stable, a phenomenon known as adsorption equilibrium.

MATERIALS AND METHODS

Study area

The cities of Kalaburagi and Bidar are part of the Kalyana region of northern Karnataka state, India, on the Deccan plateau. Kalaburagi is located at 17.4047°N and 76.6413°E, at an average altitude of 454 meters (1,490 feet) above sea level, while Bidar is located at 17.9104°N and 77.5199E, at an average altitude of 715 meters (2,346 feet) above sea level. There has been a rapid increase in the population of Kalaburagi and Bidar city, respectively, from 6.88

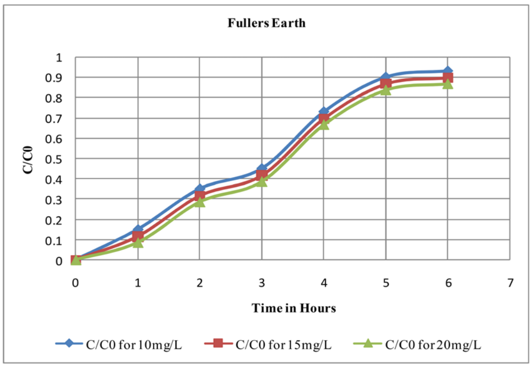

Fig 7. Break through curve for single adsorption of chromium (VI) on fullers earth for different concentrations.

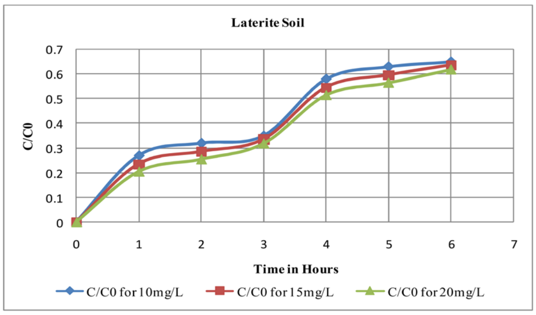

Fig. 8. Break through curve for single adsorption of chromium (VI) on laterite soil for different concentrations.

million in 2010 to 5.83 million in 2015, as a direct result of the cities' rising economic profile around the world.

This chapter's discussions revolve around the tools and methods that will be used to conduct the exhibit research, with a more thorough presentation of the design's parameters.

Selection of suitable adsorbent

Black cotton soil, which is abundant in the Gulbarga District, Laterite soil, which is abundant in the Bidar District and Fuller's earth, which is abundant in the Chincholi Taluka of the Gulbarga District, are all used as adsorbents for the removal of Cr (VI) from wastewater as shown in Figs. 2 and 3 below.

Soil samples were collected and analyzed for their physico-chemical characteristics in accordance with the relevant IS categories.

The physio-chemical characteristics of natural adsorbent and physico-chemical characteristics of waste from electroplating industry are as shown in Table 1 below.

RESULTS AND DISCUSSION

The efficiency of naturally available adsorbent in removing chromium (VI) as a function of (Joshi *et al.* 2012) (Muniyappan Rajiv Gandhi *et al.* 2012) :

Contact time
Dosage
pH

The influence of contact time, dosage and pH on Red soil, Black Soil and Fullers Earth for selected adsorbate is shown in Figs. 4, 5, 6 below.

The removal efficiency of Chromium (VI) from synthetic sample by using Fuller's earth, Laterite soil and Black cotton soil altogether is shown in Table 2 below.

Column tracer experiments (Upflow)

Chromium (VI) was used to test various adsorbents for breakthrough bends and retardation coefficients. Using Freundlich isotherm formulas, column tracer results are decoded. In all cases of Cr (VI) adsorption, the Freundlich isotherm, depicted by the equation :

$$Cads = KF \times C\frac{1/n}{aq}$$

Where,

Cads = the amount of the compound being studied that is still present in the carbon bed ;

Caq = the equal and opposite concentration of the compound in water ;

KF = the constant. with n being the Freundlich adsorption isotherm coefficients.

Substitute distribution coefficient (determined using the Freundlich isotherm)

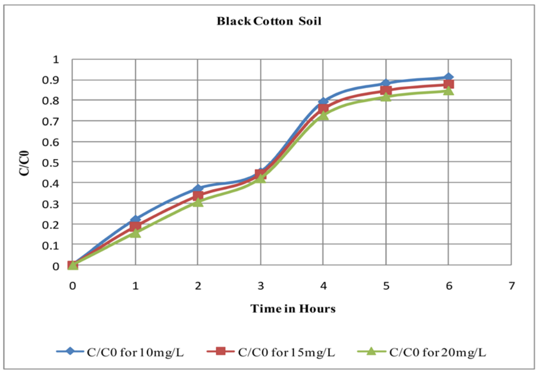

Fig. 9. Break through curve for single adsorption of chromium (VI) on black cotton soil for different concentrations.

K_d^F for a given value of balance concentration of ion adsorbed in the solution equals

$$K_d^F = \frac{K_F C_{aq}^{\frac{1}{n}}}{C_{aq}} = K^F C_{aq}^{(1/n-1)}$$

According to the adsorption isotherm, the distribution coefficient is calculated, and the retardation is defined as

$$R = 1 + \frac{Pd}{n} = *K^F D.$$

The breakthrough curves for Single Adsorption of Chromium (VI) on Fullers Earth, Laterite soil & Black cotton soil are represented in Figs. 7, 8, 9 respectively. Also the calculated values of Freundlich Coefficients for removal of Cr (VI) has been depicted in Table 3 below.

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CONCLUSION

1) Poor waste management of toxic metal-containing tailings from mining and metallurgical processes has exacerbated environmental degradation. Metals from tailings are a major source of pollution in ecological areas, especially when the wind is blowing. Toxic tailing particles can be breathed in by animals and humans during particle dispersion. These metals cause a wide variety of health problems, including developmental delays, cancer, kidney damage, endocrine disruption, immunological and neurological effects, and more.

2) Fuller's earth, laterite soil, and black cotton soil all performed well as adsorbents for the removal of Chromium (VI) from their wastewater solutions in the experiments.

3) By estimating the impact of contact time on the percentage of removal of Chromium, the kinetics of adsorption of Chromium (VI) with fuller's earth, laterite soil and black cotton soil was investigated (VI). The experimental data and results show that Chromium (VI) removal improves with longer contact times and reaches equilibrium after a fixed amount of time. For Cr (VI) adsorption, the most effective contact times for fuller's earth (70 minutes), laterite soil (110 minutes) and black cotton soil (90 minutes) are 83.5%, 69.2% and 72%, respectively.

4) Experiments conducted to determine the optimal dosage of the adsorbent showed that more adsorbent was required to completely remove Chromium (VI) from the solutions. Maximum Cr (VI) adsorption efficiency was achieved at 800 mg when using fuller's earth, 1000 mg when using laterite soil, and 1200 mg when using black cotton soil.

5) Chromium (VI) and zinc (II) adsorption are both strongly pH dependent. When the pH is lowered, adsorbent is more effective at removing contaminants. The removal efficiencies of 91.5%, 79% and 83% for Cr (VI) adsorption by fuller's earth, laterite soil, and black cotton soil are found at pH values of 2, 3 and 2 respectively.

6) Column experiments show that Chromium (VI)

adsorption is favourable, with results that are consistent with the Freundlich isotherm (1/n 1). Up flow soil column efficiency for removing Cr (VI) at 5 mg/L, 10 mg/L and 15 mg/L is 85%, 88% and 91%, respectively, when using fullers earth at these concentrations. Black cotton soil scores 78%, 81% and 84%, while Laterite soil scores 73%, 76% and 79%.

7) The time at which bed gets saturated for removal of Cr (VI) in Up-flow soil columns using fullers earth, laterite soil and black cotton soil are 6 Hrs and 9 Hrs for Fullers earth, 6 Hrs and 8 Hrs for Laterite soil and 6 Hrs and 8 Hrs for Black cotton soil respectively.

REFERENCES

Axel Arruti, Ignacio Fernandez-Olmo, Angel Irabien (2010) Evaluation of the contribution of local sources to trace metals levels in urban PM 2.5 and PM 10 in the Cantabria region (Northern Spain). *J Environ Monitoring* 12 : 1451—1458.

Barajas Aceves M, Grace C, Ansorena J, Dendooven L, Brookes PC (1999) Soil microbial biomass and organic C in a gradient of zinc concentration in soils around a mine spoil tip. *Soil Biol Biochem* 31 : 867—876.

Bisht Renu, Agarwal Madhu, Singh Kailash (2015) Removal of Chromium from Wastewater using agricultural waste : A review. ISST Journal of applied chemistry.

Chakraborty Rupa, Asthana Anupama, Singh Ajaya Kumar, Jain Bhawana, Hasan Susan Abu Bin (2020) Adsorption of heavy metal ions by various lowcost adsorbents : A review, International Journal of Environmental Analytical Chemistry.

Chao Su, Liqin Jiang, Wen ChakrabortyJun Zhang (2014) A review on heavy metal contamination in the soil worldwide: Situation, impact and remediation techni ques. *Environm Skeptics Critics* 3 (2) : 24—38.

DH Lee , YG Zo, SJ Kim (1996) Non-radioactive methods to study genetic Profiles of natural bacterial communities by PCR-single-strand-conformation polymorphism. *Appl Environ Microbiol* 62 : 3112—3120.

Ellen Sträter, Anna Westbeld, Otto Klemm (2010) Pollution in coastal fog at Alto Patache. *Northern Chile. Environ Sci Pollut Res Int* 19 : 1563—1573.

Ghani Abdul (2010) Toxic effects of heavy metals on plant growth and metal accumulation in maize (*Zea mays* L.). *Iranian J Toxicol* 3 : 325—334.

Goutom Raj, Patnaik MC, Babu PS, Kalakumar B, Singh MV, Shylaja J (2006) Heavy metal contaminants in water-soil-plant-animal continuum due to pollution of Musi river around Hyderabad in India. *Ind J Anim Sci* 76 : 131—133.

Joshi NC, Bhandari Narendra Singh, Kumar S (2012) Adsorption Behavior of Cedrus Deodara Leaves for Copper (II) from Synthetically Prepared Waste Water' , Chemistry of Phytopotentials Health Energy and Environmental Perspectives.

Mehmet Aycicek, Olcay Kaplan, Mehmet Yaman (2008) Effect of cadmium on germination, seedling growth and metal contents of sunflower (*Helianthus annus* L.). *Asian J Chemistry* 20 : 2663—2672.

Michael Aschner (2002) Neurotoxic mechanism of fishbone methylmetry. *Environ Toxicol Phamacol* 12 : 101—102.

Michael Moustakas, Thomas Lanaras (1994) 'Growth and some photosynthetic characteristics of field grown Avena sativa under copper and lead stress'. *Photosynthetica* 30 : 389—396.

Muniyappan Rajiv Gandhi, Viswanathan Natrayasamy, Sankaran Meenakshi (2012) Synthesis and Characterization of a Few Amino Functionalized Copolymeric Resins and Their Environmental Applications', Industrial and Engineering Chemistry Research.

Rajaganapathy V, Xavier F, Sreekumar D, Mandal PK (2011) Heavy metal contamination in soil, water and fodder and their presence in livestock and products : A Review. *J Environ Sci Technol* 4 : 234—249.

Susan E Bailey, Trudy J Olin, Mark Bricka R, Dean Adrian D (1998) A Review Of Potentially Low-Cost Sorbents for Heavy Metals Wat. Res 33 pp 11 : 2469—2479.

Teresa M, Vasconcelos SD, Tavares HM (1997) Trace element concentrations in blood and hair of young apprentices of a technical-professional school. *Sci Total Env* 205 : 189—199.

Uchenna Okereafor, Mamookho Makhatha , Lukhanyo Mekuto, Nkemdinma Uche-Okereafor, Tendani Sebola, Vuyo Mavumengwana (2020) Toxic Metal Implications on Agricultural Soils, Plants,Animals, Aquatic life and Human Health. *Int J Environ Res Public Health* 17 : 2204 ; doi: 10.3390/ijerph-17072204.

Van Assche F, Clijsters H (1990) 'H. Effects of metals on enzyme activity in plants'. *Pl Cell Env* 13 : 195—206.

Vhahangwele Masindi, Khathutshelo L. Muedi (2018) Environmental Contamination by Heavy Metals. Intech Open : London, UK, 2018.

Wood JM (1974) Biological cycles for toxic elements in the environment. *Science* 183 : 1049—1052.

World Health Organization (WHO) (1995) Guidelines for Drinking Water Quality World Health Organization : Geneva, Switzerland, pp 121.

Zhenli L He, Xiaoe E Yang, Peter J Stoffella (2005)Trace elements in agroecosystems and impacts on the environment. *J Trace Elem Med Biol* 19 : 125—140.