

Quality Assessment of Soil in the Vicinity of Rice Mill and Sponge Iron Industry at Central India

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ABSTRACT

Proposed study based on the biosorptive removal of chromium (III) heavy metal in the soil using a domestic plant: Cicer arietinum. This plant was selected, based on economic value and adsorption efficiency. In the column mode adsorption method, the maximum chromium (III) adsorption capacity was found as 91.72 mg/g of dry biomass. For adsorption process optimum pH and time were pH 5.0 and 60 min respectively at 26 ± 2 °C temperatures. SEM, EDX and FTIR were used to characterize the surface property of the bioadsorbent. This study was completed by optimizing various parameters like pH, initial ion concentration, biosorbent dose, contact time and temperature. NaOH is known as the best eluting agent. The research also recognized that the concentration of chromium (III) heavy metal is found very high around sponge iron comparatively rice mill.

INTRODUCTION

The soil organic matter regulates the function and quality of soil, which is a very good indicator and a dynamic medium to maintain the various biological, chemical and physical phenomenon ^[1]. The composition of soil is small fragments of broken rock, reformed by chemical and natural activities in the form of erosion and weathering ^[2]. Rice mill industry is the main agronomy industry in our country having more turn over compare to other industries ^[3]. Rice husk is produced by rice milling which bounds the paddy grain. At the time of paddy milling, approx. 78% part is obtained as unbroken and cracked rice with rice bran. The rest of 22% part is collected as rice husk. Parboiling process obtained steam by using this rice husk. 75% of the husk consist of organic volatile matter; ash is collected by another 25% parts for the period of the firing procedure ^[4].

Absorption and accumulation of heavy metal is reported with various capabilities and body parts in the plants of cropping area and also a large difference in the uptake and transformation of metals between cultivars of different and same plant species ^[5].

Basic household necessities such as feed, fuelwood, and Construction materials are heavily reliant on forests. However, forest depletion and deforestation could not be controlled as the state could not enforce rules regarding the management of forests. As a result of institutional failure, a newer concept of participatory forest management was introduced in Nepal and local people got their space created in forest management only during 1970''s with a view to mitigating forest cover loss. During the early 1990s, the government had realized the importance of long-term forestry. Natural and anthropogenic sources are responsible for the entry of heavy metals in the atmosphere. Anthropogenic sources of heavy metals in agricultural soils include mining, fertilizers, urban effluent, smelting, sewage sludge and waste disposal [6].

Commercial and household activities extremely increase the waste soil over the world [7]. Now a day, industrial effluents are using to irrigate agricultural land. As every industrial wastewater contains a special character, it may be beneficial or harmful to the crops, soils and animals of our ecosystem. Before recommend these effluents in agriculture a brief study is very important [8].

Solid, liquid as well as gaseous waste materials are generated from rice mill. Rice husk along with ash is the part of solid wastes. Though rice husk is reused for boiling of water and ash is obtained after combustion. Gaseous wastes are some harmful gases as NO_x, CO and SO₂. Rice mills also generate some liquid wastes by given procedure: paddy soaked boiler blow down and parboiling wastewater. These liquid wastes are known as effluents which are discharged to the outside of the rice mill in the common drain [9].

Discharged effluents may not be harmful to human health but it affects the water bodies. Mostly these effluents release into the nearest streams and rivers that belongs to the municipal sources [10]. These waste water reported high levels of Organic contents, COD and BOD. Organic content consists of starch and little part of rice husk [11]. Land degradation damaged to grass and cropping area because of low Organic content and pH value. Industrialization and elevated consumption of industrial product causes environmental degradation which is a dynamic problem now a day [12]. Awareness regarding clean environment is very important task for better lifestyle of human being [13]. At present, toxic elements are very serious issues, causes various health problems [14].

In Chhattisgarh Iron is the very important mineral resource. Iron ore is observed in the south west part of Chhattisgarh including following district as Rajnandgaon, Dantewada, Durg, Bastar, Kawardha, Kanker and Narayanpur. Mining activities increases soil, water and health problems continuously [15]. Sponge iron industry is growing very rapidly in India. India produces reduced iron directly in large amount, an essential part of the steel industry [16]. Iron oxide reduction causes sponge iron which is used in steel manufacturing. Steel is used to manufacture Basic Oxygen Furnace (BOF) and Blast Furnace (BF). BF produces molten iron by using smelting and refining method and BOF produces molten steel [17].

Environmental pollution because of the heavy metal, particularly in soil, is the most difficult problems due to severe noxious effect, broad distribution, exchangeable and consistency to plants compare to other pollutants which leads different diseases [18]. Sponge iron is known as raw material for manufacturing of steel and made by the reduction of iron. Coal fly ash which is discharged from the sponge iron industry consists of some heavy metals like mercury, arsenic, nickel, cadmium, lead, cobalt, zinc, copper and chromium. Thus, deposited fly ash from sponge iron industry affects the environment in the vicinity of the same industry having accumulation of above heavy metals in the top soil [19].

Heavy metals more than permissible limits are toxic because of its irregular properties leads biomagnifications. At lower concentration these toxic metals also show a variety of disorders [20]. Our aquatic eco-systems are affected by rapid growth of industry. Non-biodegradable nature of toxic elements causes serious injure to living organism [21].

Metallic compounds are constant and continuous increases in soil. Distribution of these heavy metals in cropping plants enhances the health risk via food chain while the level and adverse effect of these toxic elements to mankind beings varies by different situation. Studies have recognized that plants cultivated in contaminated soils are toxic to humans, animals and crops by using industrial effluents for irrigation [22]. Heavy metals present in soil by heavy traffic are also an important source of roadside soils [23]. Top soil is basically affected by dumped mines which influence the soil contamination. Researchers also analyses the effect of vegetation composition and succession on top soil around sponge iron industry [24].

Materials and Methods

Collection and preparation of soil

Soil is collected from the two industries of Chhattisgarh. Soil of rice mill and sponge iron is recognized as sample 1 and sample 2 simultaneously. The field was divided homogenously with the help of farmers. The surface was cleaned and litter was ploughed at the sampling site. Driving auger was used to dig the surface at 15 cm [25]. With the help of spade 'V' shaped cut of 15 cm was made to the sampling site. 15 to 20 soil samples were collected from each sampling site and stored in a tray. The samples were mixed thoroughly and waste materials like stones, gravels and roots were separated. By quartering one kg of soil will reduce. In the process of quartering thoroughly mixed soil sample divided into four equal parts [26]. Two opposite quarters will

dispose of and the left two quarters will be mixed and the process will repeat many times until sample became 1 kg. The remaining soil sample stored in plastic bags labeled with name of area, date, season and previous grown crop labeled in the bag. Then samples took in the lab and dried as well as particles like small roots, stones removed. There after soil samples grinded till 2 mm sieve. For the experiment sieved soil has been used [27].

Collection of industrial effluents

Industrial effluents discharged from the back side of industry with very bad odor. Plastic bottles are used to store effluents and labeled the name of place, industry and date. After collection effluents have been used to sieve to remove litter. At laboratory effluents are stored in air tight bottles and preserved in refrigerator for further analysis. Physical properties of effluents are given in Table 1 [28].

Table 1. The physical parameters of the Industrial effluents.

Parameters	Sample 1	Sample 2
pH	5.2	7.8
Conductivity ($\mu\text{s}/\text{cm}$)	356	389
Odor	Foul	Not
Temperature	Very high	Mid
Turbidity	7.8	7.4
BOD	80	103
DO	9.1	8.6

Plant material

Plants of *Cicer arietinum* (*C. arietinum*) were cultivated for 60 days. Five pots were filled with the soil of rice mill and another five pots were filled with soil of sponge iron. Approx 50 plants were grown in each experiment [29]. According to the concentration of heavy metals shoots of different length was observed. Well-developed leaves and stems were used for the experiment. After cultivation of two month, the leaves and stems of *C. arietinum* plant was collected and dried manually [30]. Two plants from each pot were collected for the experiment.

Collection and preparation of the biosorbent

The *C. arietinum* bioadsorbent was collected in the vicinity of two different industry of Chhattisgarh in India. Accumulated biomass was cleaned and dried manually [31]. Distilled water is used to wash it to make it pure. Then residue material was dried in oven at 60°C for few days, also the material was used to crushed and sieved through 1.18 μM to get equal-sized material for further experiment. Later, the bioadsorbent was used to clean with HCl (0.1 M) for 25 min to eliminate earlier adsorbed elements and then filtered with Whatman Filter No.42 and to make neutral washed it with distilled water. The bioadsorbent was dried at 60°C in oven. It was acknowledged that, such activities increase the grasping power of the biomass. At last, the airtight plastic container was used to store the bioadsorbent [32].

Chemicals

All used chemicals are of analytical grade and received from Merck (India/Germany). To obtain dilute solution double distilled water was used. 5% of HCl solution was used to clean all bottles and apparatus [33]. We get Cr (III) solution from equivalent nitrate salt. Chelation was reduced by using Nitrate (NO_3^{2-}) salt. pH was adjusted with 0.1 M of NaOH and HCl. Other solutions were prepared by stock solution [34].

Instrumentation

An atomic absorption spectrophotometer (iCE 3000 AA05120906 v 1.30) was used for the measurement of Cr (III). FTIR (Fourier transform infrared spectroscopy) analysis is used to identify the binding groups available in the adsorbent. FTIR (Agilent Cary 630), spectrophotometer (range 4000–4500 cm⁻¹), scanning electron microscopy (SEM, ZEISS EVO SEM 18 model), Oxford was used to analyze the physical morphology of the bioadsorbent at × 1000 magnification and chemical composition is also determined by EDX (energy dispersive X-Ray analysis, INCAEDS with X-MAX 20 mm detector). TB-214 an accurate electrical balance, vacuum filtration pump, digital ELICO pH was used for maintaining the pH of the solution [35].

Atomic absorption spectrophotometer

For any sample analysis, a very precise apparatus used to measure parts per billion of a gram (µgdm⁻³). This instrument is based on the absorption of a specific wavelength by an element. Movement of electron from lower to upper energy level requires some energy. 50 to 4500 m distance is selected to collect the soil sample from the rice mill and power plant industry (Figure 1) [36]. Table 2 and 3 shows the concentration of Chromium in soil sample and Figure 1 shows relation between conc. of Cr (III) and distance in m.

Figure1. Graph plotted between conc. of Cr (III) and distance in m (series 1 indicates rice mill industry and series 2 indicates sponge iron industry).

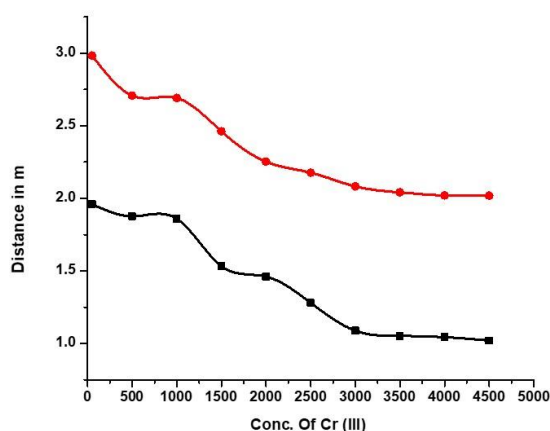


Table 2. Concentration of Cr (III) ion around the Rice mill industry.

Distance in m	50	500	1000	1500	2000	2500	3000	3500	4000	4500
Conc. of Cr (III) ion	1.960	1.876	1.860	1.534	1.462	1.280	1.089	1.052	1.043	1.021

Table 3. Concentration of Cr (III) ion around the sponge iron industry.

Distance in m	50	500	1000	1500	2000	2500	3000	3500	4000	4500
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Conc. of Cr (III) ion	2.984	2.708	2.692	2.462	2.253	2.177	2.083	2.041	2.020	2.019
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Batch mode adsorption study

The batch adsorption analysis was performed at the temperature of $26 \pm 2^\circ\text{C}$. In every set, 3 g of biomass was mixed with the solution of chromium at various concentrations; at pH and contact time fixed at 5 and 60 min respectively. Later, the vacuum filtration pump was used to filter the mixture by through $0.45 \mu\text{M}$ Millipore filter paper. Concentration of chromium was observed by the help of AAS. Earlier than analysis, instrument was calibrated by standard Cr (III) solution [37].

Column adsorption study

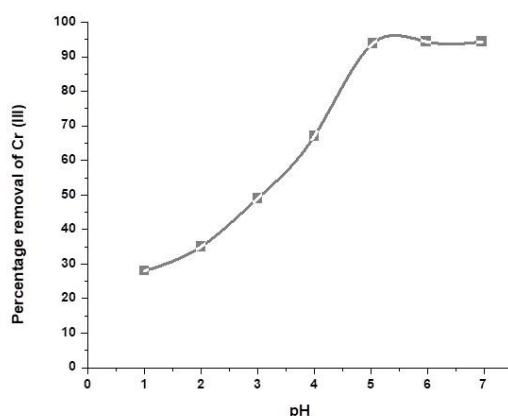
Packed column adsorption study enhances the binding capacity of metal considerably compare to batch mode. Therefore, room temperature ($26 \pm 2^\circ\text{C}$) is suitable for column adsorption study [38]. The column of glass with 4 cm diameter and 36 cm height was used for the experiment. Two sets were prepared for the analysis. Both columns were filled with approx 50 gm of biomass collected from the rice mill and sponge iron industry. Two sides of both columns were supported by stones. Experiment was allowed to moisten the biomass via double-distilled water. After that the Cr (III) solution having 140 mg/l of concentration of and pH 5.0 was constantly flowed through the column with the help of peristaltic pump and 15 ml/min was fixed as flow rate. This procedure was repeated till the biosorption arrived to the saturation point in the column mode adsorption [39].

RESULTS AND DISCUSSION

Effect of pH on biosorption

The pH plays an immense role in the uptake of Cr (III). In this study, removal of Cr (III) was considered at a various pH range (2.0-8.0) with fixed concentration (140 mg/l) of Cr (III), 3 g/100 ml biosorbent dosage and contact time of 60 min. It was established that pH 5.0 was chosen as optimum for the percentage removal of Cr (III) increases shown in Figure 2 and further percentage removal of Cr (III) decreases. Precipitation takes place after pH 8.0.

Figure 2. Graph plotted between pH and percentage removal of Cr (III).

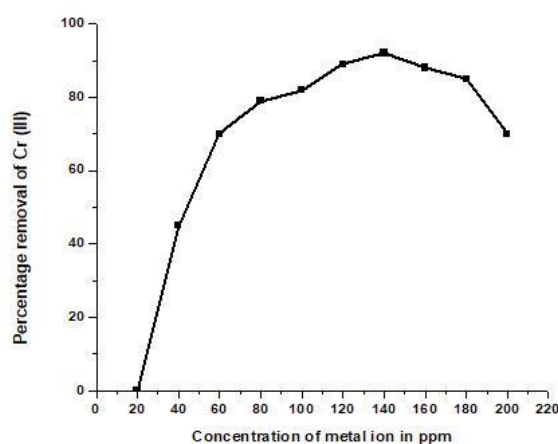


Effect of metal ion concentration

The concentration of Cr (III) was tested in the range of 100 to 500 mg/l with pH 5.0, the biosorbent dose 3.0 g/100 ml

and fixed contact time of 60 min. Batch study shows that the removal of Cr (III) metal ion decreases from 100 to 95%, when the concentration of Cr (III) metal ion was increased from 100 to 500. Removal of Cr (III) metal ion can be seen in Figure 3.

Figure 3. Relation between concentration of metal ion and percentage removal of Cr (III).



Effect of Biosorbent dosage

Biosorbent dosage affect the removal of Cr (III) which is identified by varying the dosage of adsorbent till the range of (1–8 g/l) and fixed initial concentration of chromium metal ion (140 mg/l) at pH of 5.0. Experiment shows that no remarkable change is observed for the removal of Cr (III) after 3.0 g/100 ml. Therefore, 3.0 g/100 ml was selected as the optimum biosorbent dose.

Effect of contact time

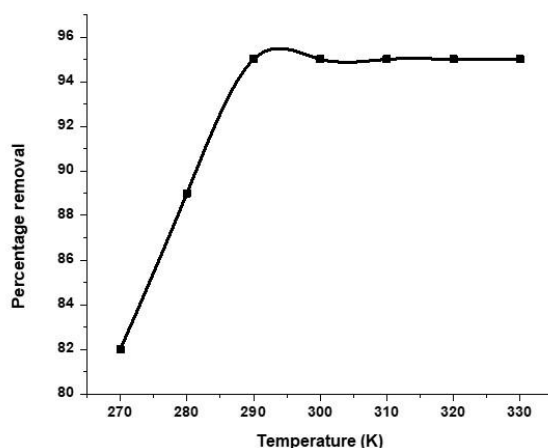
Contact time is very important for the effective removal of the heavy metals. The contact time was tested in the range of 30-120 min followed by optimized parameters. In this experiment, the percentage removal of Cr (III) metal ion increases from 70 to 90% when the fixed contact time increases from 30 to 60 min. Results shows that the adsorption rate is observe very high at the beginning as a number of active sites is present for the process of adsorption. Maximum percentage of removal was obtained understating of the 60 min. If we increase contact time more than 110 min it was not become very beneficial. Thus, the contact time was optimum as 60 min.

Effect of temperature

The effect of temperature was studied in the range of 273 K-330 K. The experiments were held to find the temperature effect on chromium (III) adsorption at 273 K, 283 K, 293 K, 303 K, 313 K, and 323 K temperatures. Figure 4 shows the graph plotted between the experimental data and percentage removal of Cr (III) heavy metal. It is identified that percentage removal of heavy metal increases with temperature and it became constant after 293 K. Thus, 293 K was

optimum.

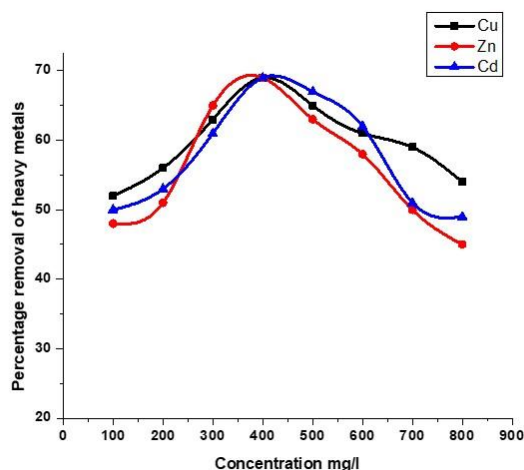
Figure 4. Relation between temperature and percentage removal of Cr (III)



Effect of co-ions

Presence of some co-ions like Cd (II) and Cu (II) decreases the percentage removal of Cr (III) (Figure 5). Zn (II) also affect negatively at low concentrations. According the above experiment co-adsorption of some cations like Cd and Cu carried with Cr ions. Hence the presence of such cation causes a tough competition for the availability of active sites as well as decreases the removal of chromium ions. Some cations like Fe (II), Mn (II), Ni (II) and Pb (II) never affect the percentage removal of chromium. Same as, some anions like arsenate, chloride, nitrate, phosphate and sulphate did not affect the removal of chromium ions.

Figure 5. Relation between concentration of co-ions and percentage removal of Cr (III).



Desorption studies

Batch system carried the desorption study of the absorbed Cr (III) ions using bioadsorbent. Elution of Cr (III) was held through NaCl, 0.1 N HNO₃, 0.1 M Na₂CO₃, HCl and NaOH reagents. Where, the pH, bioadsorbent dose and equilibrium time of the solution was observed 5.0, 3 g/100 ml and 60 min consequently. Result shows that the effect of various eluting reagent for desorption. NaOH is known as the best eluent compared to the other reagent (Supplementary Figure 1d). Approx 85% of Cr (III) heavy metal was removed from NaOH reagent, whereas other reagents are not more effective.

FTIR method

FTIR is the best method to identify the involved functional group in the adsorption process. Figures 6 and 7 shows the functional group present in adsorbent before and after adsorption around rice mill.

Figure 6. FTIR spectra of native biomass.

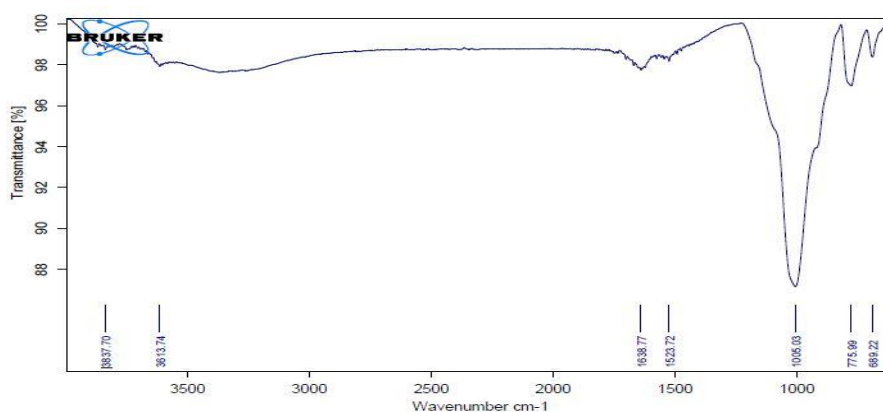
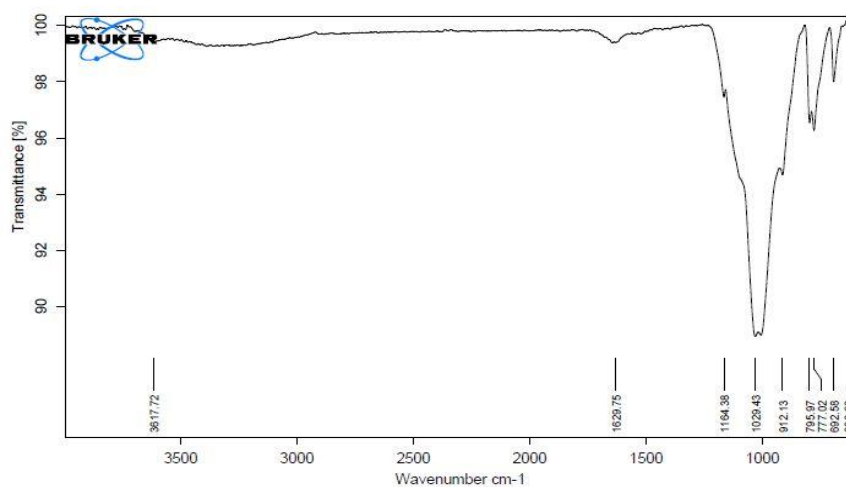


Figure 7. FTIR spectra of Cr (III) loaded biomass from rice mill industry.



The adsorption peaks around 3200-4000, 3700-3584 and 1690-1640 cm⁻¹ represents C=O, O-H stretching and amine/oxime functional group corresponding. IR peak around 1650-1100 cm⁻¹ and 1225-950 cm⁻¹ shows Secondary amine

NH bend and Aromatic C-H in Plane bend. Some other peaks represents functional groups as 915–890 cm^{-1} Vinyl C-H out of Plane bend, 600-800 cm^{-1} C-Cl stretch band, 675-1000 cm^{-1} =C-H bending, 850-550 cm^{-1} C-Cl stretch band, 690-515 cm^{-1} C-Br stretch band. Summary of the functional group is given in Table 4.

Table 4. FTIR data of native and loaded biomass collected from rice mill industry

S. No.	Native biomass(cm^{-1})	Metal loaded biomass (cm^{-1})	Change in peak behaviour of loaded biomass	IR peak range (cm^{-1})	Functional group reported corresponding To the observed peak behaviour (cm^{-1})
1	3837.7	3817.72	shift	3200-4000	C=O
2	3613.74	Not present	Disappear	3700-3584	OH stretching
3	1638.77	1620.75	Shift	1690-1640	Amine/oxime
4	1523.72	1164.38	shift	1650-1100	Secondary amine NH bend
5	1005.03	1029.43	Shift	1225-950	Aromatic CH in plane bend
6	Not present	912.13	Disappear	915-890	Vinyl C-H out of Plane bend
7	775.99	795.97	shift	600-800	C-Cl stretch Bend
8	689.72	777.02	Shift	675-1000	=C-H bending
9	Not present	692.58	Disappear	850-550	C-Cl stretch Bend
10	Not present	630.83	Disappear	690-515	C-Br stretch band

In the same way some FTIR peaks is also observed in the adsorbent collected from sponge iron. Figure 8 and Table 5 represent the FTIR spectra of adsorbent before and after adsorption. IR peak range was observed for specific functional group. 3200-4000 cm^{-1} C=O, 1650-1100 cm^{-1} Secondary amine NH bend, 1690-1640 cm^{-1} amine/oxime, 1650-1100 cm^{-1} Secondary amine NH bend, 675-1000 cm^{-1} =C-H bending, 600-800 cm^{-1} C-Cl stretch band, 675-1000 cm^{-1} = C-H bending, 850-550 cm^{-1} C-Cl stretch band, 680–610 cm^{-1} Alkyn C-H bend.

Figure 8. FTIR of Cr (III) loaded biomass from sponge iron industry.

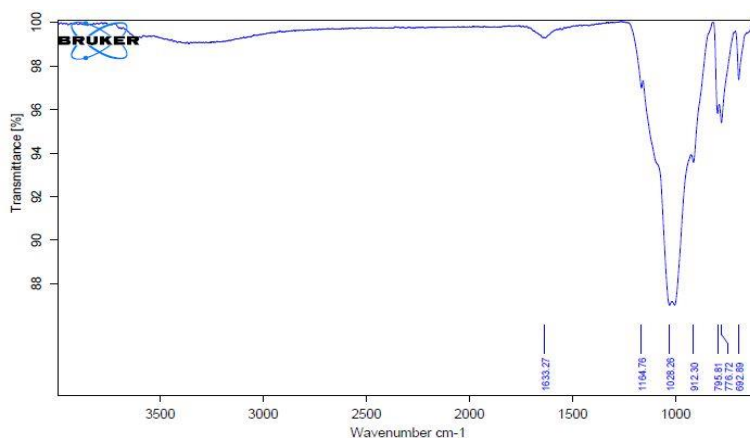


Table 5. FTIR data of native and loaded biomass from sponge iron industry.

S. No.	Native biomass (cm ⁻¹)	Metal loaded biomass (cm ⁻¹)	Change in peak behavior of loaded biomass	IR peak range (cm ⁻¹)	Functional group reported corresponding To the observed peak behavior (cm ⁻¹)
1.	3837.7	Not present	Disappear	3200-4000	C=O
2.	3613.74	Not present	Disappear	3600-3650	Free O-H stretching
3.	1638.77	1633.27	Shift	1650-1100	Secondary amine NH bend
4.	1523.72	1164.76	Shift	1525-950	Aromatic C-H in-plane bend
5.	1005.03	1028.26	Shift	1650-1100	Secondary amine bend
6.	Not present	912.30	Shift	675-1000	=C-H bending
7.	775.99	795.81	Shift	600-800	C-Cl stretch band
8.	689.72	776.72	Sift	675-1000	=C-H bending
9.	Not present	692.89	Shift	850-550	C-Cl stretch band
10.	Not present	630.83	Disappear	680-610	Alkyne C-H bend

SEM and EDX analysis

SEM and EDX are used to identify the surface morphology and chemical composition of the bioadsorbent consequently. Figure 9(a) shows the SEM and EDX image of control biomass. Supplementary Figure 9 (b) and (c) shows the SEM and

EDX image of *C. arietinum* biomass at × 500 magnification collected around the rice mill and sponge iron consequently. Image clearly proves that bioadsorbent consist of a large number of pores and grooves with irregular shape which is accomplished for the adsorption of Cr (III) heavy metal. While the EDX picture of *C. arietinum* bioadsorbent collected from the same field consists of C, O, Ca, Mg, Si, Cl and K atoms rather than Cr (III) given in Table 6. Cr (III) heavy metal is absent in native biomass but present in loaded biomass. It is also identified that concentration of Cr (III) heavy metal is high in the vicinity of sponge iron industry compare to rice mill industry (Table 6).

Figure 9. a) SEM and EDX of control biomass; b) SEM and EDX of Cr (III) loaded biomass of rice mill industry; c) SEM and EDX of Cr (III) loaded biomass of sponge iron industry.

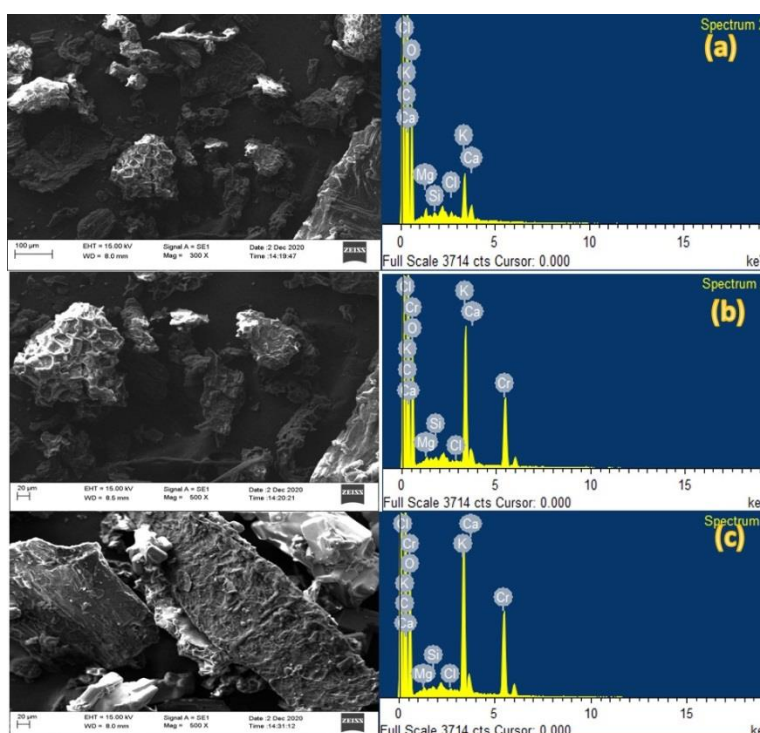


Table 6. Elemental composition of control and chromium (III) loaded biomass.

Elements	Rice mill				Sponge iron			
	Native		Cr loaded		Native		Cr loaded	
	Weight	Atomic	Weight	Atomic	Weight	Atomic	Weight	Atomic
C %	23.41	30.94	14.24	23.47	23.41	30.94	11.48	19.56
O %	64.06	63.56	48.27	59.73	64.06	63.56	48.56	62.1
Ca %	2.57	1.02	1.24	0.61	2.57	1.02	0.73	0.37

Mg %	1.28	0.83	0.46	0.38	1.28	0.83	0.39	0.33
Si %	0.46	0.26	0.35	0.25	0.46	0.26	0.25	0.18
Cl %	0.95	0.43	0.32	0.18	0.95	0.43	0.23	0.13
K %	7.27	2.95	16.07	8.14	7.27	2.95	17.14	8.97
Cr (III) %	-	-	19.05	7.25	-	-	21.21	8.35

Behavior of column mode adsorption study

Batch mode adsorption as well as column mode adsorption study explored very useful parameters. The column mode adsorption study is recognized more efficient due to the higher removal efficiency of heavy metal with rapid output. In the process of column mode adsorption operation, adsorbent is thoroughly kept in contact with Cr (III) solution. Therefore, the Cr (III) solution came in contact with the adsorbent in a column remained comparatively constant. To observe the efficient result for removal of Chromium by column mode, the experimental setup was optimized as mentioned earlier. Concentration of the chromium solution used for the experiment was 140 mg/l with the flow rate of 15 ml/min. Bed volume and Empty Bed Contact Time (EBCT) was calculated by using eq. (1) and (2)

$$\text{Bed Volume} = \pi r^2 l \quad (1)$$

Where r indicates the radius of the column and l shows the bed length.

$$\text{EBCT} = \text{Bed Volume} / \text{Flow rate (ml/minutes)} \quad (2)$$

Approx 30 l of chromium solution was used to pass through the column containing 50 g of the adsorbent. 0.04 mg/l was observed as initial point on passing at 0.5 L of the metal solution. Final quantity of chromium solution passed was 27 l.

This equation was used to calculate the removal capacity of the column

$$\text{Removal Capacity (mg /g)} = (C_i - C_f / M) * V$$

Where C_i=initial metal concentration (mg/l)

C_f=final metal concentration (mg/l)

V=Volume of solution (l)

M=Mass of the sample (gm).

All the data of the column study is shown in Table 7.

Table 7. Parameters of column study.

Metal	Concentration (ppm)	Flow rate (ml/min)	Bed volume (min)	EBCT	Removal capacity (mg/g)
Cr (III)	140	15	350.51	30.78	91.72

Adverse effect of high concentration of chromium (III)

Cr (III) is responsible for multiple chronic diseases. Recent years a large number of people are affected by various diseases. Waste water enters into farmland area. It can be reduced by proper crop and soil management. The high level of heavy metals accumulated in crops especially in rice crops affected to human health. Name of diseases caused by Cr (III) heavy metal is given in Table 8.

Table 8.Chronic effect of Cr (III) heavy metal on human being.

S. No.	Clinical effect	Primary sources	References
1.	Nephritis, anuria and extensive lesions in kidney and gastrointestinal ulceration	Coal field area	(22)
2.	Cancer	Agricultural area	(25)
3.	Cancer, hypertension, fever, kidney disorder	Agricultural soil	(26)
4.	Ulcer, Perforation of Nasal Septum, Res	Industrial dust and fumes and polluted food	(28)
5.	Mouth ulcers, indigestion, acute tubular necrosis, vomiting, abdominal pain, kidney failure and even death	Earth's crust	(29)

Application of biomass (*C. Arietinum*) for removal of chromium from industrial effluents

Proposed work was further applied for the removal of Cr (III) from the effluent, was collected from cement industry and located in Chhattisgarh (India). After sample collection double distilled water was used for dilution of sample. The same experiment was repeated for the bioadsorbent after adsorption of Cr (III) as above method. Satisfactory results were found, shown in Tables 9,10.

Table 9. Comparative study of different bioadsorbent for removal of Cr (III) heavy metal.

S. No.	Name of bioadsorbent	Plant sample	Reference
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1.	<i>Cicer arietinum</i>	Leaves and stems	This paper
2.	<i>Prosopis laevigata</i>	Shoot and root	(30)
3.	<i>Typha angustifolia L</i>	Leaves and roots	(31)
4.	<i>Halimione portulacoides</i>	Root	(32)
5.	<i>Convolvulus arvensis L</i>	Leaf	(33)
6.	<i>Eichhornia crassipes</i>	Root and shoot	(34)
7.	<i>Zea mays</i>	Shoot, fruit and root	(35)
8.	<i>Pluchea indica</i>	Root, stem and shoot	(36)
9.	<i>Helianthus annuus, Cynodon dactylon, Panicum virgatum</i>	Root and shoot	(37)
10.	<i>Sorghum bicolor (L.)</i>	Root and leaf	(38)
11.	<i>Avena sativa L.</i>	Grain, straw and roots	(39)
12.	<i>Leersia hexandra Swartz</i>	Leaf	(40)

Table 10. Physical properties of effluents from cement industry

Parameters	Concentration (mg/l) before adsorption	Concentration (mg/l) after adsorption	Removal of heavy metals (%)
pH	3.11 (adjusted 5 pH)	6.9	-
Lead	4.6	0.11	86.4
Cadmium	49.6	2.3	71.2
Copper	58	5.72	87
Arsenic	4.8	0.52	81
Chromium	5.1	0.49	93.2
Nickel	76.5	13.7	88.2
Zinc	89	21.4	64.5

CONCLUSION

Proposed work confirms *C. arietinum* biomass as an effective bioadsorbent for the removal of Cr (III) from industrial effluents. Efficiency of adsorption in batch mode and column mode were observed as 22.72 mg/g and 60.72 mg/g respectively. The highest percentage removal of Cr (III) heavy metal was observed 96% at optimized condition.

Characterization by FTIR indicates that the amine group, alkanes, carboxyl functional groups and halogen group were responsible for chromium binding. Some surface phenomena of adsorbent are identified using SEM and EDX analysis. SEM and EDX image of the native and loaded biomass (around rice mill and sponge iron) shows that the concentration of chromium heavy metal in soil around rice mill found comparatively less than the soil around sponge iron. For the regeneration of the biomass desorption study of the NaOH explained *C. arietinum* as a good eluting agent.

Declarations

This manuscript has not been published and it is not under consideration for publication elsewhere, it does not contain plagiarized.

Author conflict of interest

The authors declare that they have no conflict of interest.

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