Retraction

Retraction: Remediation of Cr(VI) from wastewater using biochar of Indian Grass (IOP Conf. Ser.: Mater. Sci. Eng. 1145 012115)

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This article (and all articles in the proceedings volume relating to the same conference) has been retracted by IOP Publishing following an extensive investigation in line with the COPE guidelines. This investigation has uncovered evidence of systematic manipulation of the publication process and considerable citation manipulation.

IOP Publishing respectfully requests that readers consider all work within this volume potentially unreliable, as the volume has not been through a credible peer review process.

IOP Publishing regrets that our usual quality checks did not identify these issues before publication, and have since put additional measures in place to try to prevent these issues from reoccurring. IOP Publishing wishes to credit anonymous whistleblowers and the Problematic Paper Screener [1] for bringing some of the above issues to our attention, prompting us to investigate further.

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Remediation of Cr(VI) from wastewater using biochar of Indian Grass

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Abstract
Chromium is extremely noxious unneeded for any living organism and its occurrence is unusual in nature. Many industrial activities such as mining, metal plating, wood preservation, dyes, pigments, tanning and textile industries makes pollution which cause major health hazards. The present study explores the possibilities using biochar from any carbonized material to use as source to remove the toxic material from any industrial effluent and particularly for Cr(VI). Batch process was accomplished to examine the outcome of various parameters to eliminate the Cr (VI) from the solutions. The rate of adsorption has been interrelated with all the parameters. The Cr(VI) adsorbed bio-char may be used as a fuel in Ferrochrome industry. From the study, it was experimental that adsorption kinetics obeys the pseudo second order kinetics. Experimental data follows the Langmuir isotherm. Intra-particle diffusion is most sluggish steps which determine the rate.

Keywords: Cr(VI), Biochar, uptake, kinetics, isotherm;

1. Introduction
The chromium is important material is used commonly in metallurgy, electroplating and other manufacturing units and that release the chromium into the environment [1-3]. Adsorption process is right process for the elimination of toxic metal when the unwanted metal concentration is lower in quantity [4-5]. A essential character of good adsorbent is their large surface area and high porosity. From the literature, it is evident that bio-sorbents have high Cr(VI) uptake capacity as compare to other adsorbents. However, the disadvantages with the bio-sorbent is that, the uptake is higher at lesser pH, treatment at lesser pH requires neutralization steps which are not economic and environmental friendly and regeneration is not possible because of adsorption cum reduction mechanism [6]. Therefore, the present study aimed at finding an alternative adsorbent i.e. biochar to eradicate the Cr(VI) from the wastewater and use this chromium adsorbed biochar. The researchers indicated that the potential for 18-40% mitigation of CO2. Apart from the CO2 reduction, the charcoal based iron making reveals following benefits to the process. Biochar contains less sulphur and phosphor content than coke.

1. Low ash content compared to coke.
2. As because of high porous with more surface area which improves combustion rate.

Biochar addition is very small percentage so the effect of cost will be negligible. To explore the result of various factors on adsorption, batch studies were done by changing the parameters to eliminate of Cr(VI) from the solutions by using this Biochar.
2. Methods
The batch adsorption experiment was conducted in a beaker at isothermal condition using a magnetic agitator with speed regulator. The required samples were collected under dynamic condition at standard time intermissions and filtered through a filter paper. Percentage adsorption (E%) and uptake (qe) of Cr(VI) has been analysed by UV spectrophotometer and determined by using following equations (1) and (2),

\[ E\% = \frac{(C_0 - C_f)}{C_0} \times 100 \]  
\[ q_e = \frac{V(C_0 - C_f)}{W} \]  

3. Result and Discussion
3.1. Outcome of contact time
The batch process is carried out to obtain the equilibrium interaction time. The batch processes executed for 10 hours and kept all other parameters were constant during the experimentation. The outcomes are shown in Figure 1 shows that adsorption was very rapid for first 45 minutes and almost 80% adsorption has been reached during this phase as because of available surface area. Once free surface is occupied, adsorbed Cr molecules penetrate to the pores present in the adsorbent. Equilibrium is achieved within 10 hours in this process and so the left over studies were executed for 10 hrs.

3.2. Outcome of Initial pH of Solution
The initial pH is a greatest influential parameter disturbing the adsorption process [7]. Under the constant stirring speed, pH has been varies between 2 and 4.0 to study the impact on percentage of adsorption. The outcomes are shown in Figure 2 below. From the experiments, it is clear that percentage adsorption as well as the uptake capacity of the adsorbent increases with decrease in pH. The reason behind in increasing in adsorption capacity with decrease in pH may be due to at low pH, the surface turn into more positive because of presence of large number of H+ ion.

The percentage adsorption as well as Cr(VI) uptake capacity was maximum at pH 1.0 however, the effluent after adsorption is highly acidic pH of 2.2. Acidic effluent is not environmental friendly and hence required acid neutralization steps. Further, neutralization of effluent can lead to increase in total solid and this may not be cost effective process.

It was perceived that the maximum removal (100 %) was at pH of 2.0 and 2.5. The uptake capacity increased from 10.7 mg/g at pH of 4.0 to20 mg/g at pH of 2.0. Even though, maximum capacity observed to be at pH 2.0, but the effluent from the process will be highly acidic and hence required acid neutralization steps which may not be cheap to run and environmental welcoming [8]. Further, the used adsorbent may not be suitable for recycle to the ferrochrome industry, if the treatment carried out at such lower pH. Therefore, the remaining studies were done at pH of 3. The final pH of the effluent of the process increased to more than 5.

3.3. Effect of Initial Cr(VI) Concentration
The concentration at the beginning of Cr (VI) is also another major factor affects the percentage of adsorption and also the uptake. The outcomes were shown in Figure 3. It is experiential that, by increasing the initial concentration, the percentage of adsorption is increasing, as because of more active sites present in the adsorbent. The adsorption increases the maximum to 100% at 10 ppm has decreased to
94% at 100 ppm of initial Cr (VI) concentration. But the uptake is increased from 2 mg/g at 10 ppm to 18.9 mg/g at 100 ppm as because of increase in the energetic dynamism to conquer all the resistances among the solution and solid phases.

3.4. Effect of Adsorbent Dose
The adsorbent dose also varied under the concentration of initial Cr (VI) solution was 10 ppm for all further studies, remaining all other adsorption parameters were kept constant under constant stirring speed. The outcomes were depicted in Figure 4. From the graph it is observed, the kinetics was rapid in the beginning 30 minutes, after that adsorption becomes slower. During the rapid phase, 90% of the removal has taken place. The process reached steadiness within 360 minutes, after that not much changes in concentration. The percentage of removal was increased from 59% at dose of 1 g/L to 100% at 10 g/L as because initially more active sites present in the adsorbent were exposed [9,10]. The uptake has reduced from 5.9 to 1.42, once the dose increased from 1 g/L to 10 g/L.

4. Kinetic Model
In order to design a continuous column for the removal of Chromium from effluent it is essential to find the rate at which adsorption proceeds. In the present study batch data has been fitted with various [11] kinetic models i.e. Laguerre’s model, Ritchie’s model, First Order Reversible and Pseudo second order were used.

These model equations are extensively applied in the adsorption in heterogeneous adsorption particularly for in a liquid solution by using kinetic equations [12] given as in Equations 3-6

\[ \ln(q_t - q) = \ln q_e - kt \]  
Ritchie model equation

\[ \frac{q_t}{q_e} = 1 + kt \]  
For the reversible reaction, this generally expressed as

\[ \ln(1 - V_t) = -(k_{\text{forward}} + k_{\text{backward}})t \]  
Pseudo second order kinetics

\[ \frac{t}{q} = \frac{1}{k_2q_e^2} + \frac{1}{q_e} \]

The constant values together R² are assessed and stated in Table 1. It is clear from the table it follows pseudo second order model. The kinetic parameter and R² has been tabulated in Table 1.

5. Equilibrium Adsorption Isotherm
The mechanism of adsorption by the biochar was studied through the data were fitted to various isotherm models. The experimental data have been used to fit in Langmuir isotherm, Freundlich isotherm [12] and Temkin isotherm [13]. This is outlined below given as in Equations 7-9.
\log q_e = \log K_p + \frac{1}{n} \log C_e \quad (8)

\frac{q_e}{b} = \frac{RT}{b} \ln A + \frac{RT}{B} \ln C_e \quad (9)

All the constant value and interpreted values are stated in the Table 2. From that it obeys the Langmuir model based on the R² values and also the mechanism of the process.

6. **Rate Controlling Mechanism**

The rate controlling mechanism on spongy nature of adsorbents is controlled in four steps. The first step is bulk diffusion i.e. movement of Chromium in solution to solid adsorbent. Then followed by that is film diffusion which is mass transfer controlling step. Third one is surface diffusion. Finally, the intra-particle diffusion is takes place. Out of these either one or multi steps may control the rate. The experiment was carried out in enough speed so, bulk and film diffusion may not be a controlling steps. The adsorbent used in our experiment is permeable. The diffusion takes place in porous structure [14-15]. can be construed as below

\[ q_t = k_{id} t^{1/2} \]

where \( q_t \) is adsorbent uptake and \( k_{id} \) is intra-particle diffusion coefficient. The graph between \( q_t \) versus \( t^{1/2} \) gives the value of \( k_{id} \). Results of all tests were tabulated Table 3.

7. **Conclusion**

The adsorption capacity of the many of the bio-sorbent is low at higher pH. Further the bio-sorbent neither can be regenerated nor can be used directly in any industrial process. Therefore, in the present study explore usage of adsorbent biochar for the treatment of Cr (VI). The advantages of using Biochar as an adsorbent is that the used Biochar can be reused in a ferrochrome industry as a source of carbon i.e. fuel. Further, the adsorbed Cr (VI) can be used as a raw material for the ferrochrome production. Therefore, no regeneration or disposal of the adsorbent is required which may create environmental problem and hence can be treated as clean treatment technology [16]. The adsorption experiments were carried by varying different parameters to find out their effects on the percentage adsorption as well as uptake of the adsorbent. As usual, the adsorption capacity and percentage adsorption increases with decrease in pH. The percentage adsorption increases with increase in adsorbent dose whereas, the uptake capacity decrease with increase in adsorbent dose. In case of increase in adsorbate concentration, the percentage adsorption decreases whereas the uptake capacity increases. The entire process followed second order kinetic model and Langmuir isotherm. The surface diffusion is found to be the rate limiting step.

From the literature few adsorbents were chosen and results were related in Table 4 and can be concluded that current adsorbent is similar with numerous adsorbents stated in the literature.
Figure 1. Effect of contact time Condition: Concentration: 100 ppm, Dose: 5 g/L, Temp: 30°C

Figure 2. Effect of pH Condition: Concentration: 10 ppm, Dose: 5 g/L, Temp: 30°C

Figure 3. Effect of Initial Cr(VI) Concentration. Condition: pH 3.0, Dose: 5 g/L, Temp: 30°C.

Figure 4. Effect of Adsorbent Dose. Condition: pH 3.0, Concentration: 100 ppm, Temp: 30°C
Table 1. Adsorption Kinetic models parameters

| Parameter               | Values       | Pseudo 1st order | Richie's 2nd order | Pseudo 2nd order | First order reversible |
|-------------------------|--------------|------------------|--------------------|------------------|------------------------|
|                         |              | k     | R²    | k     | R²    | k₁    | k₂    | R²    |
| Dose (g/L)              |              |       |       |       |       |       |       |       |
| 1                       |              | 0.316 | 0.87 | 0.08  | 0.61  | 0.040 | 0.973 | 0.026 | 0.180 | 0.740 |
| 3                       |              | 0.360 | 0.904| 0.16  | 0.53  | 0.130 | 0.995 | 0.047 | 0.200 | 0.790 |
| 5                       |              | 0.640 | 0.97 | 1.1   | 0.74  | 0.253 | 0.999 | 0.470 | 0.050 | 0.921 |
| 7                       |              | 0.511 | 0.833| 0.45  | 0.91  | 0.500 | 0.999 | 0.070 | 0.360 | 0.860 |
| 10                      |              | 0.640 | 0.91 | 0.952 | 0.81  | 1.020 | 0.999 | 0.050 | 0.304 | 0.910 |
| pH                      |              |       |       |       |       |       |       |       |       |
| 2                       |              | 0.67  | 0.88 | 0.853 | 0.87  | 0.003 | 0.999 | 0.040 | 0.002 | 0.890 |
| 2.5                     |              | 0.42  | 0.99 | 0.17  | 0.94  | 0.002 | 0.999 | 0.012 | 0.001 | 0.826 |
| 3                       |              | 0.4   | 0.88 | 0.19  | 0.42  | 0.003 | 0.997 | 0.010 | 0.002 | 0.932 |
| 3.5                     |              | 0.39  | 0.95 | 0.19  | 0.97  | 0.005 | 0.998 | 0.004 | 0.006 | 0.977 |
| 4                       |              | 0.38  | 0.85 | 0.413 | 0.36  | 0.009 | 0.996 | 0.010 | 0.007 | 0.903 |
| Initial Concentration(ppm) |          |       |       |       |       |       |       |       |       |
| 10                      |              | 0.661 | 0.97 | 1.1   | 0.74  | 0.253 | 0.999 | 0.020 | 0.002 | 0.810 |
| 25                      |              | 0.4   | 0.98 | 1.3   | 0.33  | 0.042 | 0.999 | 0.010 | 0.002 | 0.840 |
| 50                      |              | 0.4   | 0.923| 0.3   | 0.64  | 0.010 | 0.997 | 0.008 | 0.002 | 0.960 |
| 100                     |              | 0.4   | 0.88 | 0.400 | 0.42  | 0.003 | 0.997 | 0.008 | 0.002 | 0.930 |
Table 2. Adsorption isotherm models parameters

| Parameter          | Values | Freundlich Isotherm | Langmuir Isotherm | Temkin Isotherm |
|--------------------|--------|---------------------|-------------------|-----------------|
|                    |        | Slope(1/n) | log Kf | R²  | 1/q_max | R²  | RT/b | R²  |
| Dose (g/L)         | 1      | 0.116       | 0.64  | 0.84 | 0.17    | 0.999 | 1.39 | 0.799 |
|                    | 3      | 0.094       | 0.65  | 0.78 | 0.342   | 0.999 | 0.590 | 0.756 |
|                    | 5      | 0.027       | 0.002 | 0.614| 0.5     | 0.999 | 0.216 | 0.734 |
|                    | 7      | 0.023       | 0.1   | 0.565| 0.7     | 0.999 | 0.344 | 0.900 |
|                    | 10     | 0.020       | 0.17  | 0.632| 1.000   | 0.999 | 0.181 | 0.945 |
| pH                 | 2      | 0.264       | 1.144 | 0.638| 0.05    | 0.999 | 3.19 | 0.760 |
|                    | 2.5    | 0.33        | 1.46  | 0.620| 0.05    | 0.999 | 3.52 | 0.800 |
|                    | 3      | 0.266       | 1.34  | 0.510| 0.053   | 0.999 | 2.67 | 0.680 |
|                    | 3.5    | 0.35        | 1.27  | 0.645| 0.067   | 0.999 | 2.63 | 0.770 |
|                    | 4      | 0.270       | 1.03  | 0.490| 0.094   | 0.999 | 1.51 | 0.660 |
| Initial Concentration(ppm) | 10 | 0.161       | 0.144 | 0.635| 0.50    | 0.999 | 0.216 | 0.730 |
|                    | 25     | 0.211       | 0.64  | 0.68 | 0.203   | 0.999 | 0.685 | 0.780 |
|                    | 50     | 0.21        | 0.97  | 0.602| 0.103   | 0.999 | 1.27 | 0.740 |
|                    | 100    | 0.197       | 0.970 | 0.491| 0.05    | 0.999 | 2.28 | 0.623 |
### Table 3. Rate controlling mechanism

| Parameter                  | Values | $q_t$ vs $t^{1/2}$ | $q_t/q_e$ vs $t^{1/2}$ | $\ln(1-(q_t/q_0))$ vs $t$ |
|----------------------------|--------|--------------------|------------------------|--------------------------|
|                            |        | $k_d$ mg/g min$^{1/2}$ | $D_1$ mm$^2$/time $10^{-6}$ | $D_2$ mm$^2$/time $10^{-3}$ | $R^2$ | $D_2$ mm$^2$/time $10^{-3}$ | $R^2$ |
| Adsorbent dose (g/L)       | 1      | 1.480              | 0.974                  | 0.92                     | 0.87  | 0.160                     | 0.279 | 0.950 |
|                            | 3      | 1.484              | 0.98                   | 1.55                     | 0.984 | 0.340                     | 0.593 | 0.990 |
|                            | 5      | 0.710              | 0.97                   | 0.88                     | 0.972 | 0.340                     | 0.593 | 0.934 |
|                            | 7      | 0.650              | 0.95                   | 1.72                     | 0.99  | 0.380                     | 0.663 | 0.980 |
|                            | 10     | 0.370              | 0.9                    | 1.72                     | 0.993 | 0.340                     | 0.593 | 0.954 |
| pH                        | 2      | 0.91               | 0.66                   | 8.07                     | 0.97  | 1.300                     | 2.267 | 0.900 |
|                            | 2.5    | 1.13               | 0.78                   | 3.58                     | 0.95  | 0.400                     | 0.698 | 0.950 |
|                            | 3      | 1.23               | 0.912                  | 5.78                     | 0.995 | 0.564                     | 0.984 | 0.930 |
|                            | 3.5    | 1.05               | 0.883                  | 5.78                     | 0.92  | 0.550                     | 0.959 | 0.980 |
|                            | 4      | 0.69               | 0.915                  | 4.78                     | 0.99  | 0.980                     | 1.709 | 0.910 |
| Initial Concentration (ppm)| 10     | 0.084              | 0.69                   | 4.78                     | 0.94  | 0.900                     | 0.570 | 0.980 |
|                            | 25     | 0.23               | 0.79                   | 5.07                     | 0.98  | 0.390                     | 0.680 | 0.995 |
|                            | 50     | 0.55               | 0.91                   | 3.29                     | 0.983 | 0.060                     | 1.203 | 0.994 |
|                            | 100    | 1.235              | 0.91                   | 5.47                     | 0.99  | 0.564                     | 0.984 | 0.930 |
| S.No | Adsorbent                  | Time (min) | pH     | Adsorbate conc. (mg/L) | Dosage (g/L) | Temp. °C | % Ads. | Uptake (mg/g) |
|------|---------------------------|------------|--------|------------------------|--------------|----------|--------|---------------|
| 1    | Bael shell                | 240        | 2      | 50                     | 10           | 30       | 92     | 17.27         |
| 2    | Basillus Biomass          | 480        | 2      | 100                    | 1            | 30       | 15     | 14.9          |
| 3    | Rice Husk                 | 360        | 1.5    | 25                     | 10           | 25       | 25     | 12.17         |
| 4    | Rice Straw                | 180        | 2      | 25                     | 10           | 25       | 25     | 11.39         |
| 5    | Magnetite nanoparticle    | 60         | 2.5    | 50                     | 5            | 25       | 25     | 15.3          |
| 6    | Neem leaves               | 240        | 2      | 50                     | 10           | 25       | 25     | 15.95         |
| 7    | Sulfonated Lignite        | 60         | 10     | 25                     | 25           | 25       | 25     | 27.87         |
| 8    | Bromide micellar          | 60         | 2      | 25                     | 25           | 25       | 25     | 17.89         |
| 9    | Neem bark                 | 482        | 6.5-7  | 4-5                    | 1            | 10       | 100    | 19.6          |
| 10   | Husk of Pomegranate       | 240        | 3      | 150                    | 3            | 25       | 25     | 35.2          |
| 11   | Coconut shell             | 600        | 3      | 100                    | 5            | 20       | 20     | 18.9          |

Table 4. Assessment of the Biochar with several adsorbents stated in literature.
References

1. Gupta V.K., Rastogi A., Nayak A., Removal of Cr(VI) from aqueous solutions by adsorption onto hazelnut shell activated carbon: kinetic and equilibrium studies, *Bioresour. Tech.*, 91 (2004) 317–321.

2. Saroj Sundar Baral, Kavitha Mohanasundaram & Surendran Ganesan, Selection of suitable adsorbent for the removal of Cr(VI) by using objective based multiple attribute decision making method, *Preparative Biochemistry & Biotechnology*, 69-75, 20 Jul 2020, https://doi.org/10.1080/10826068.2020.1789993

3. Sharma I., Dinesh G., Kinetic modeling: Chromium(III) removal from aqueous solution by microbial waste biomass, *J. Scientific Ind. Res.* 68 (2009) 640-646.

4. Surendran G., & Baral, S.S. Biosorption of Cr(VI) from wastewater using Sorghastrum Nutans L. Nash. *Chem. Ecol.*, 34(8) (2018) 762-785.

5. A. Saravanan, V. Brindha, R. Manimekalai, S. Krishnan, An evaluation of chromium and zinc biosorption by a sea weed (Sargassum sp.) under optimized conditions, *Ind. J. Sci. Technol.* 2 (2009) 53-56.

6. A Netzer, Hughes, D.E. Adsorption of copper, lead and cobalt by activated carbon. *Water Res.* 18 (1984) 927–933.

7. Baral, S.S., Surendran, G., Das, N., Rao, P.V., Statistical design of experiments for the Cr(VI) adsorption on weed salvinia cucullata, *Environ. Engg. Manage.J.*, 12 (2013) 465-474.

8. Goel R.P., Smelting Technologies for Ferrochromium Production-Recent Trends, Ferro Alloy Industries in the Liberalised Economy, (1997) 37-50.

9. Ariyama T., Murai R., Ishii J., Sato M., Reduction of CO2 emissions from integrated steel works and its subjects for a future study, *ISIJ Int.*, 45 (2005) 1371–1378.

10. Matheickal J.T., Yu Q., Bio-sorption of lead from aqueous solutions by marine algae Ecklonia radiate, *Water Sci. Technol.*, 34 (1996) 1–7.

11. S, D., & H, A. (2019). AODV Route Discovery and Route Maintenance in MANETs. 2019 5th International Conference on Advanced Computing & Communication Systems (ICACCS). doi:10.1109/icaccs.2019.8728456

12. H. Anandakumar and K. Umamaheswari, An Efficient Optimized Handover in Cognitive Radio Networks using Cooperative Spectrum Sensing, Intelligent Automation & Soft Computing, pp. 1–8, Sep. 2017. doi:10.1080/10798587.2017.1364931

13. Ho Y.S., Review of second-order models for adsorption systems, *J. Hazard. Mater.*, 36 (2006) 681-689.

14. Davis T.A., Volesky B., Mucić A., A review of the bio-chemistry of heavy metal bio-sorption by brown algae, *Water Res.* 37 (2003) 4331-4330.

15. Pearse C.L., Lloyd J.R., Guthrie J.T., The removal of colour from textile waste water using whole bacterial cells: a review, *Dyes Pigments*, 58 (2003) 179-196.

16. Baral S.S., Das N., Chaudhary R.G., Das S.N., A preliminary study on the adsorptive removal of Cr(VI) using seaweed, *Hydrilla Verticillata*, *J. Hazard. Mater.*, 171 (2009) 358-369.