Process Design For Removal of Heavy Metals By A Bio-sorbent Trickle Bed System: A Proof of Concept

Prashant Kumar¹, Sudeep Asthana², Ram Singh Purty¹, Sayan Chatterjee¹*
¹University School of Biotechnology, Guru Gobind Singh Indraprastha University, New Delhi 110078.
²School of Chemical Engineering and Physical Sciences, Lovely Professional University, Phagwara, Punjab 144411.
*corresponding author: sayan@ipu.ac.in

Abstract. Most heavy metals are well-known toxic and carcinogenic agents and when discharged into the wastewater represent a serious threat to the human population and the fauna and flora of the receiving water bodies. The development of a novel biofilter was aimed in this project. The various parameters of the biofiltration processes, their mechanism for heavy metals removal along with the efficiency of the biofilters and its scale up aspects have been studied. The work was targeted towards removal of Iron (Fe) and Chromium (Cr), two very common contaminant in urban as well as rural ground water. These are also found in industrial spent waters. The efficiency of the biofiltration process for heavy metals removal have been critically analysed. In a proof-of-concept study, a laboratory-scale closed biofilter system employing the trickle bed process was operated to remove Iron (Fe) and Chromium (Cr) from a synthetic waste water sample at a load of 1000mg/L of the heavy metal. Gravel, citrus peels and spent tea leaves after proper pre-treatment was used as filter media. Depth profile analysis of the filter bed showed the reduction of a steep gradient of Iron and Chromium from the top layer to the bottom layer of filter media in the biofilter. Iron and Chromium level at the bottom of the biofilter decreased over 85% over a period of 6-8 hours of experiment. With these observations we have scaled up the process from a 0.050 L to 15.0 L operating volume. The results were consistent.

1. Introduction

Water crisis tops the list of the difficulties which restrict the sustainable development of the world. The scarcity of water resources available for the use of mankind is very limited in number. It is also due to severe droughts and increasing energy costs. For the restoration of environment, water crisis remains one of the obstacles which need to be tackled. Water reuse is now considered to be an important step towards conservation of water resources. It has also been considered as an important initiative towards decreasing global water resource risks. Therefore, it is the need of the hour to introduce certain kind of bio filters which can remove the contaminants and make the water reusable. The potential of such filters for wastewater management is yet to be commercially exploited in most of the regions of the world. Several technologies for wastewater treatment include adsorption, oxidation and high-pressure membrane filtration, but they are expensive. On the contrary, biological filtration systems are typically simple and robust [1]. In developing countries, poor operations and maintenance of the sewage treatments have been observed which further leads to pollution of water resources. As a result, the country faces serious health and socio-economic threats to the population. Efforts must be taken to reuse and recycle the available water bodies as the solution of water shortage [2].

For the treatment of wastewater, different chemical and physical methods are used for the treatment of wastewater such as biological degradation, adsorption, ion exchange, chemical precipitation, coagulation, flocculation, reverse osmosis etc [3].
On human health, when considering the rate of intake, it is known that Cr (III) is badly absorbed. Therefore, because of the existence of Cr (VI) type, the toxic nature of chromium happens. The skin, lungs, and gastrointestinal tract can absorb it readily. Reducing Cr (VI) is a detoxification method when it happens for poisonous or for genotoxic impact at a distance from the target site, while reducing Cr (VI) may be used to activate chromium toxicity when it happens in or near the target organ cell nucleus. If Cr (VI) is extracellularly decreased to Cr (III), this type of metal will not be transferred easily into cells and therefore toxicity will not be noted. The equilibrium between extracellular Cr (VI) and intracellular Cr (III) eventually dictates the quantities and rates at which Cr (VI) may enter cells and impart their toxic impacts [4, 6]. Very little free iron circulates in the bloodstream under normal conditions. Iron bound to proteins such as transferrin prevents it from causing damage. The levels of free iron can increase significantly in the body and lead to iron toxicity. Free iron may cause harm to cells since it is a pro-oxidant, the inverse of antioxidant [5, 6].

2. Method and materials

2.1 Chemical reagents
For analytical use and pretreatment for the process, the following analytical grade reagents were used - sulphuric acid, orthophosphoric acid, 1,5-diphenyl carbazide solution, hydrochloric acid, hydroxyamine hydrochloride solution, ammonium acetate solution, 1,10-phenanthroline solution, potassium dichromate, ferrous sulphate, acetone and activated charcoal.

2.2 Bio materials
Based on the previous studies [7-11], the peels of sweet lime, spent tea leaves and gravels were used to design the multistage adsorption process. The gravel bed acted as a Trickle bed to allow settling of soil, dirt and dust particles in the bed before the process fluid enters the sorption columns. The biosorption beds were constituted by pre-treated citrus peel bed and spent tea leaves in succession.

2.2.1 Pre-treatment and preparation of Citrus peel bed
The peels of the sweet lime were collected from a juice shop in the neighboring locality at regular intervals. The peels were cleaned thoroughly which included removing the remaining pulp from the peels and twigs or other waste material. Then, the peels were placed in an incubator set at 60°C for 3 days until the peels were completely dry and brittle. The peels were then broken into smaller pieces with the help of a rolling pin and finally grinded to coarse particles in the mixer grinder. This powder was then sieved through to get the coarse particles separated from the fine particles using a woven wire sieve of mesh size 125 mm-20 µm. These coarse particles were collected and used in the column. Then the extra dried coarse particle samples were stored in the air tight container to preserve the growth of microbes for later use.

2.2.2 Pre-treatment and preparation of adsorption bed from spent tea leaves
After use the waste tea leaves were collected from a local tea stall located within the university campus at regular intervals. The leaves were collected after one round of its use. They were then washed thoroughly and dried in the incubator at 60°C. This exercise was repeated 4 times to make sure that the tea leaves did not retain any coloured pigments. Then the dried samples were stored in the air tight container to preserve the growth of microbes for later use.

2.2.3 Preparation of a gravel bed
Very fine gravel (Granule) of size range 2-4 mm was collected from the playground of children near community hall in the University campus. It was sieved to remove the unwanted stones and impurities using a regular woven wire sieve. Then it was stored in air tight container to prevent it from impurities.

2.3 Reaction design
The reaction was performed in a small scale to check its potential to absorb heavy metals from waste water. To begin with 50 ml Tarson / Falcon tubes were taken. It is packed with 4 different layers i.e., gravel sand, sweet lime peels, spent tea leaves and activated charcoal. A scaled-up volume of 10 L were used in a reaction column with varied bed height of the Bio-sorbents.

2.4 Performance analysis
In order to check the performance of the scaled-up system against the popular water quality parameters, we have measured the COD, TDS, pH, residual Iron and chromium content as per the national standard of FSSAI protocols [12].

2. Results and discussions

3.1 Reactor configuration
The reactor was designed to accommodate multilayer of packing with an aspect ratio (L:D) of 2:1 for all individual beds. We had earlier observed the proof of concept for 3 layer packing namely gravel, citrus peels and spent tea leaves in equal proportion in a 50 ml Tarson / Falcon tube.

The volume of our reactor was:
\[
V = \left( \pi \times R^2 \times H_1 \right) + \left\{ \frac{1}{3} \times \pi \times r^2 \times H_2 \right\}
\]
Where R, inner radius of the cylinder = 9.5cm , 
\(H_1\), Height of the cylinder = 50cm, 
\(R\), inner radius of the cone = 9.5cm 
\(H_2\), Height of the cone = 9.0cm
Thus, \(V = 14176.436 + 842.080 = 15019 \text{ cm}^3 = 15.019 \text{ litres}\)

Packed volume = Total volume – Void volume = 15.019 – volume of water required to completely fill the packed bed = (15.019 – 5.0) litre = 10 L
Void fraction = 5/15 = 0.3,
Average residence time = 20 min

In order to observe the relative effect of the bio-sorbents in the synergistic system, we evaluated the performance of the bio-sorbent column with varied proportion of bio-sorbent bed heights namely- only gravel (as control), only citrus peels, only tea leaves and the varied ratio of citrus peels : tea. For Iron bio-sorption, a ratio of 1:1 of citrus peels : tea leaves were found to be the best with the lowest residual iron found in the system after 12 hours as 450 ppm (Figure 1). Similarly, in case of Chromium it was again observe that the ratio of 1:1 recorded the lowest residual chromium after 10 hours as 130 ppm (Figure 2).
The performance of the scaled up system was thus optimized at the bio-sorption bed ratio of 1:1 and a residence (reaction) time of 12 hours for further evaluation against the popular water quality parameters where we have measured the COD, TDS, pH, residual iron and chromium content (Table 1). The results indicated appreciable improvement in the water quality parameters suitable for municipal usage.

**Figure 1.** Iron (Fe$^{3+}$) biosorption by the biofilter at different bed height of citrus peel and spent tea leaves over time

**Figure 2.** Chromium biosorption by the biofilter at different bed height of citrus peel and spent tea leaves over time
Table 1: Performance analysis of the proposed reactor

| Parameters   | Our packed bed reactor                      |
|--------------|---------------------------------------------|
| COD          | 1390 to 640 ppm                             |
| TDS          | 1150 to 530 ppm                             |
| pH           | 5.4 to 6.8                                  |
| Odour        | None                                        |
| Metal ions   | Cr - 1000 ppm to 130 ppm                   |
|              | Fe - 1000 ppm to 450 ppm                   |
| Colour       | reddish yellow to transparent               |

The results were very promising as compared to the recent reports on metal adsorption by leaves and peels [13 – 16]. Combination of both these bio-sorbents to treat iron and chromium simultaneously had been indicative of use of combinatorial approach with these bio-sorbents for more efficient metal removal.

3. Conclusions

Bio-sorbents are popular methods to biologically treat waste waters. The use of non-microbial bio-sorbents, especially for water treatment, is gaining more momentum. We have tried to use two such biomaterials in synergy in our adsorption system. To the best of our knowledge, this is the first report on combinatorial approach with both these bio-sorbents to treat iron and chromium simultaneously. The results showed an indicative change in the reduction of Iron and Chromium content. However, to attain potable quality of water, further treatment process needs to be added at the downstream of this process. It can be inferred that our method will definitely lessen the load on the further downstream processing for potable water to a large extent.

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