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Pre-analysis of heavy metals followed by biochar application as a strategy for removal of heavy metals from water of River Ravi: A comparative study

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Pakistan which was once water rich country has turned into a water starved country as the major water resources of the country are continuously depleting. This rapid decline in the fresh water resources both qualitatively and quantitatively needs to be addressed on urgent basis and new water treatment techniques must be developed to secure the fresh water resources. In this study we compared the heavy metals removal efficiency of two methods; i-e, Biochar technique which is a relatively new method and the precipitation method which is one of the conventional heavy metals removal techniques. For this purpose, samples of River Ravi were taken from four different points at two different depths which were pre and post analyzed for 8 heavy metals. Biochar method proved to be a more efficient and cost effective method as it caused 100% removal whereas precipitation method managed to remove only 75-80% of heavy metals. Metals like Fe, Pb and Ni which make complex hydroxides had only 50% removal after precipitation. One- way ANOVA was applied which has statistically proven that biochar method is more efficient as well as cost effective in removing heavy metals.

Keywords: Heavy metals, Biochar, Adsorption, Precipitation, Water treatment.

INTRODUCTION

Population of the world according to the latest census has reached 7.349 billion and still counting. This rampant increase in population is augmenting pressure on fresh water resources of the world. Along with increasing population, rapid urbanization, industrialization and increased agricultural practices are also playing their part in the destruction by polluting the fresh water resources. Most of the industries throw untreated waste water into fresh water bodies. Industrial effluents as well as surface runoff has the highest content of heavy metals which is directly dumped into rivers, lakes etc.The extreme toxicity, non-biodegradability and abundance in manmade and natural environments of heavy metals pose a great threat to human health. Among them lead, arsenic, mercury, chromium, nickel, cadmium and copper are the most toxic and carcinogenic. Their presence in fresh water could result in dreadful environmental and health related issues (Inyang et al. 2016). River Ravi which once used to be a jewel in the crown of Lahore has over the time become polluted to such extent that it has now become a menace for the environment of Lahore. River Ravi has become the most polluted river in Pakistan owing to the indiscriminate disposal of untreated municipal sewage as well as industrial effluent from the industrial units of Kala Shah Kaku, Sheikhupura Road, Kasur, Township and Gulberg industrial Estate of Lahore (WASA sources). There are about 14 major drains which collects the sewage and industrial waste water and dump into River Ravi. Ravi is receiving almost 1307.08 tons of hazardous effluents and untreated waste on daily basis (EPD, 2010). The

per capita waste water generation in Lahore is estimated to be 231 lpcd. About 3304 cusecs of untreated waste water is dumped into River Ravi only by Lahore (JICA, 2010). This unchecked dumping of untreated sewage and industrial effluents into Ravi is destroying the water quality by contaminating it with various pollutants including high content of heavy metals (WASA Sources, 2013). In developed world, almost 70% of the industrial waste is directly dumped into fresh water courses (UN Water, 2017) but these developed nations have tactfully handled this issue and the concept of using Biochar for waste water treatment has actually moved from novelty to ubiquity. In developed countries, Biochar is not only being used as a fertilizer or in waste water treatment but also in construction and paper industry. The water resources of Pakistan have decreased from 1299 m^3/capita in 1995-97 to 1100 m^3/ capita in 2006 and it is projected to become less than 700 m^3/ capita by 2025. This rapid drainage of resources has turned Pakistan into a water starved country. Therefore, there is a huge requirement of treating waste water to make it of further use (Shahzad, 2016). Out of approx. 190 million population of Pakistan, around 60 percent of urban and 80 percent of rural population does not have access to clean water, mostly having heavy metals concentration exceeding NEQS. This inaccessibility of clean and treated water is the major reason behind 100 million registered cases of various water borne diseases. According to a latest survey, every 2 out of 5 persons are dying every day because of drinking polluted water. Therefore, there is a need of introducing new and cost effective waste water treatment techniques in Pakistan (Shahzad, 2016). Many methods have been developed so far to address the issue of heavy metal contamination of fresh water resources. Out of Conventional water treatment methods/ strategies, Precipitation, Ion exchange, Membrane filtration, Electro-coagulation, Phytoremediation etc are the most effective methods in removing heavy metals from waste water however most of these do have high operational cost and sludge disposal issues (Chavda and Pardya, 2014). These drawbacks gave a considerable impetus to the development of an alternate low cost waste water treatment method especially in Pakistan.

Biochar, a pyrogenic carbon rich material is prepared through the pyrolysis of any kind of organic waste including agricultural waste, household/ kitchen waste, sewage sludge etc. Biochar has so far been recognized as a multi-functional material with various agricultural and environmental applications but due to its unusual adsorptive capability it could also prove to be a promising, highly efficient and cheap sorbent for different pollutants (Foereid, 2015). The concept of using Biochar for waste water treatment is in its developing stage in Pakistan. This research has not only provided a method of managing huge amount of biomass/ waste but also a cheap alternate for industries to treat waste water. Treated waste water could be reused for agricultural purposes and the heavy metals/ nutrients laden Biochar could again be used as a fertilizer. Precipitation is basically to create solids from a solution. Chemicals are added in the solution which with the help of the gravitational force bring the solid particles together and make them settle at the bottom as 'Precipitates'. The chemicals which are added to make the solids precipitate are called the 'Precipitants'. The precipitate free liquid after the precipitation is known as the 'Supernatant or Supernate'. Precipitation usually occurs when the concentration of a compound exceeds its solubility and is more rapid in supersaturated solutions (Gunatilake, 2015). Chemical precipitation is an old and the most commonly used technique particularly for the removal of heavy metals and some anions from waste water. Because of its effectiveness and efficiency in removing heavy metals, precipitation technique has its application in almost every sector. The aim of this technique is to precipitate the required heavy metal from waste water by converting it into an insoluble form by adding any reagent or chemical (Gunatilake, 2015). Precipitation technique can be used for both positive and negative ions. The conventional precipitation process includes Hydroxide Precipitation and Sulphide Precipitation.

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MATERIALS AND METHODS

This research was done in the water of River Ravi. A comparison of the efficiency and effectiveness of precipitation, a traditional heavy water removal technique from waste water was made with the relatively new Biochar method. Samples were collected from River Ravi and analyzed.

Sample Collection

A total of 16 water samples were taken from 4 sampling stations viz. near Mehmood booti/Ravi siphon (S1), near Bund road (S2), near Batti chowk (S3) and Saggian Ravi Bridge (S4) at two different depths in evening

mostly near or around sewage and industrial drainage. 8 of the samples (with three replications) were treated through Biochar method (T1) and the other 8 (with three replications) through the precipitation method (T2). The samples were pre analyzed for heavy metals including Zn, Cu, Cr, Pb, Fe, Ni, Mg and Mn.

Preparation and Application of Biochar Treatment

For producing Biochar, two types of waste including Rice husk and Wheat straw were taken. Waste was washed by distilled water and then dried in oven at 70° C for 24 hrs. Waste was then pyrolyzed (fast pyrolysis) in a muffle furnace at a rate of 25° C/ min until it reaches 450°- 500 C. This temperature was fixed for 225 minutes (Ouyang et al. 2014). Pyrolyzation took place in the absence of oxygen. Once the Biochar was prepared, it was cooled, crushed and sieved after steam activation. pH of Biochar before application was 8.1.(Pan et al. 2015). Suspensions (w/v) of water samples were prepared by dissolving approx. 0.5-1 g of Biochar in almost 100 ml of sample and shaken for 24 hrs (Pan et al. 2015). The suspensions were kept for two weeks in lab and then again analyzed for heavy metals using Polarized Zeeman Atomic Absorption Spectrophotometer (model Z-8230). Both pre and post analysis readings were compared.

Application of Precipitation Treatment

The other eight samples were treated using precipitation method. Heavy metals were precipitated from samples in the form of hydroxides by using sodium hydroxide. About 5% sodium hydroxide solution was added drop wise in the samples (Gunatilake, 2015). pH was continuously monitored using pH meter (HI 2210 HANNA). Precipitation occurred in all the samples between the pH ranges 6.5- 11.The samples were re analyzed after precipitation and the amount of heavy metals was quantified again using Atomic Absorption Spectrophotometer.

RESULTS AND DISCUSSION

Biochar caused 100% removal of heavy metals. Metals like Fe, Pb and Ni which can form complex hydroxides and increase their solubility were also completely removed whereas precipitation technique managed to cause only 75%- 80% of removal. Metals like Fe, Pb and Ni had only 50% removal. The Figures 1 and 2 clearly showed that heavy metals were detected in large quantities at the depth as compared to the samples collected from surface mainly because of the proper mixing and settling down of metals at the bottom.

Quantities of heavy metals were different at all sampling stations as it is clearly shown by figures 1 and 2. Chromium was not detected at any sampling station as it is a major tannery pollutant and there were no tanneries in the surroundings. Metals like Cu, Zn and Mn were found in extremely less quantity while Mg, Fe, Pb and Ni were detected in higher quantities Maximum values were found near Bund Road and Batti Chowk area while minimum values were found at Ravi Siphon. Among heavy metals Mg was found in the highest quantity mainly because of the domestic and industrial activities in the vicinity Biochar method totally removed these metals at all sampling stations. Tan et al. 2015 used Biochar for removing heavy metals from aqueous solution and achieved almost 80 % of removal efficiency. Precipitation technique managed to remove 75% of heavy metals at points where the quantities of Zn, Cu and Mn were a bit higher. 100% removal levels were only achieved at points where the metals were already in minimal quantities. It can clearly be seen in figures 3 and 4. Biochar method was an extremely cost effective method for removing heavy metals as there were no chemicals or other experimental equipment required. Biochar was prepared from organic waste which was of no further use and the heavy metal laden Biochar could again be used as a fertilizer or soil amendment, therefore, it proved itself to be a cheap method of waste recycling and management as well. Foereid (2015) found Biochar method not only very efficient in removing heavy metals but also an extremely cheap technique. On the other hand, precipitation method was not that much cost effective as there were chemicals and equipment required and was less efficient as compared to the Biochar method.

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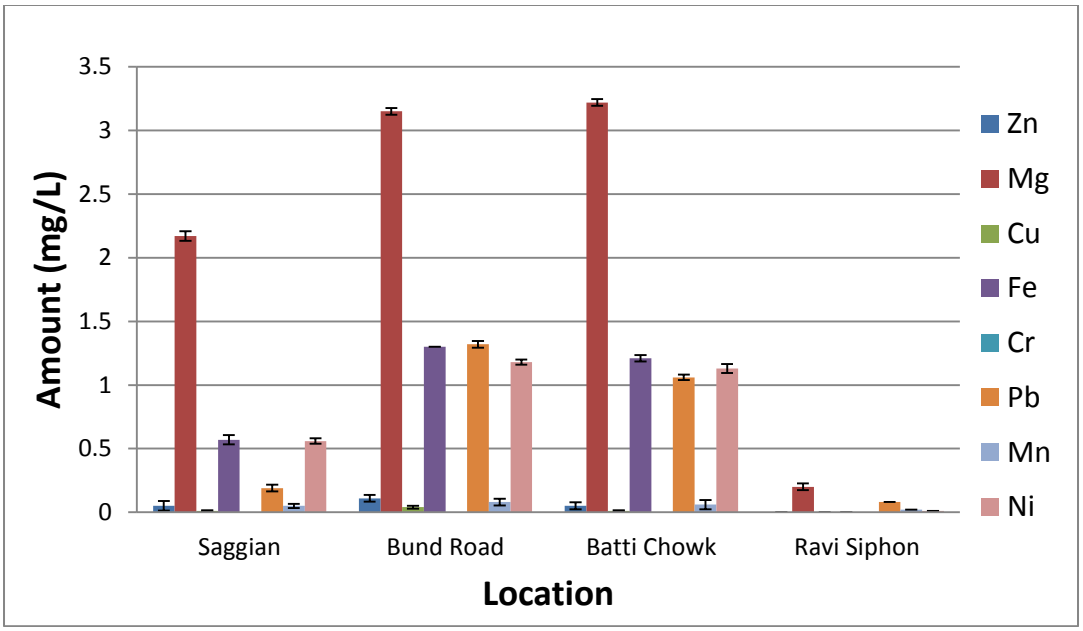

Figure 1. Pre Analysis of heavy metals at surface

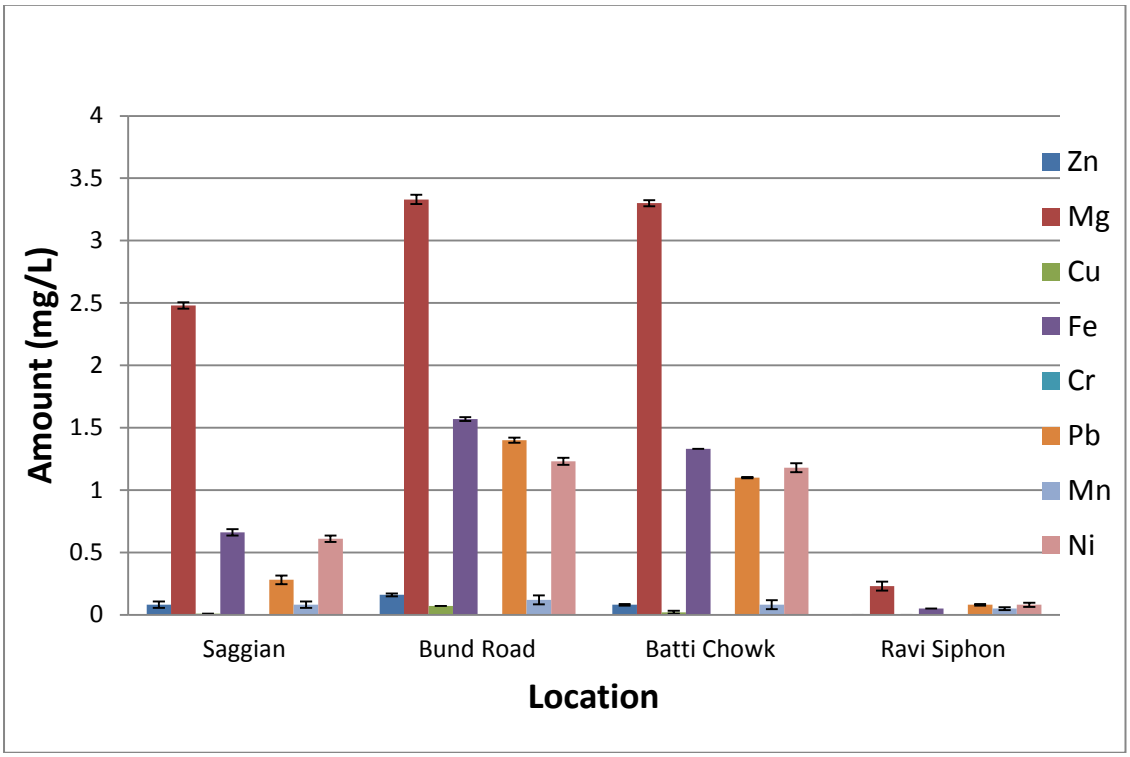

Figure 2. Pre analysis of heavy metals at depth

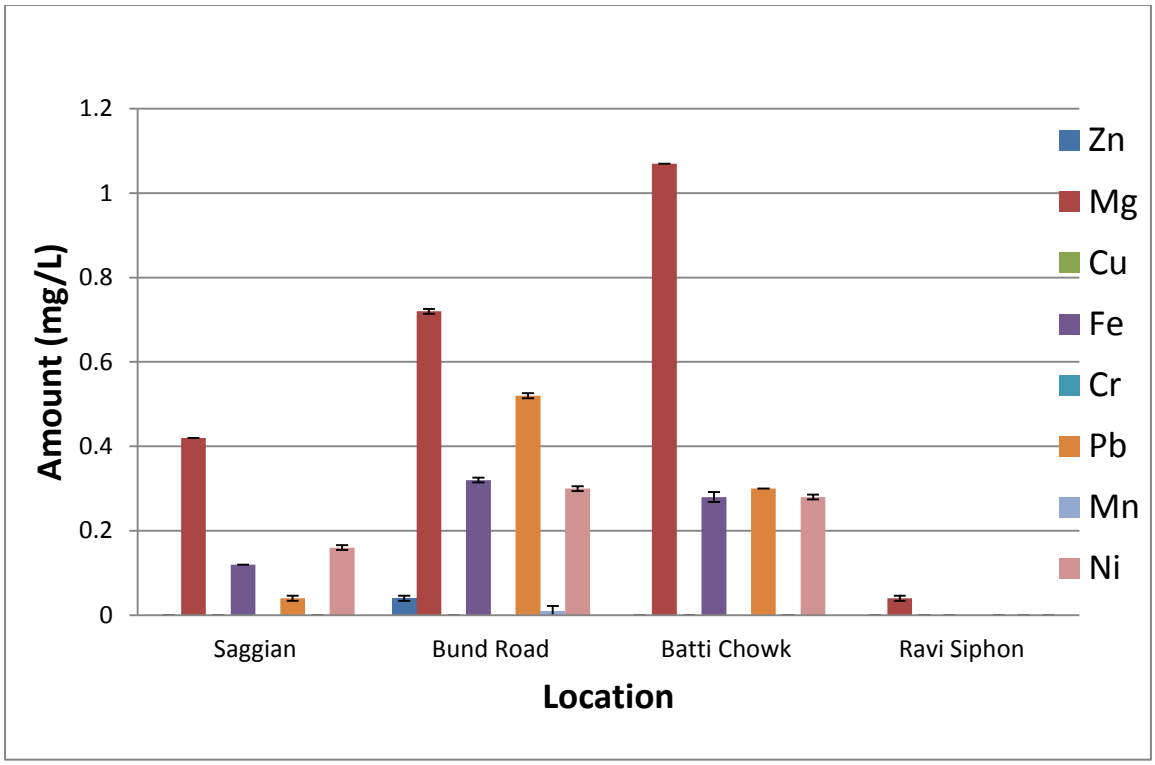

Figure 3. Post Analysis of heavy metals at surface- Precipitation

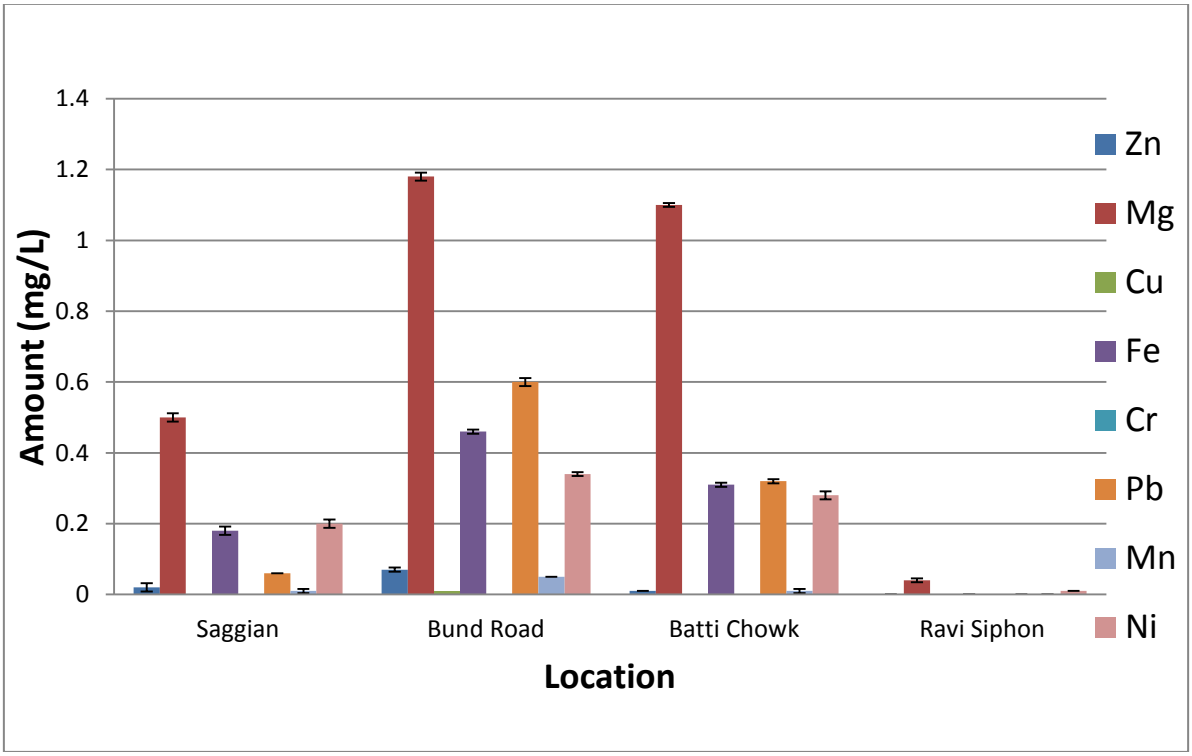

Figure 4. Post Analysis of heavy metals at depth- Precipitation

Table 1. Summary of statistical analysis

No.	Metal	α- Value	p- value after Biochar method	p- value after precipitation method
1	**Cu**	0.05	0.032	0.045
2	**Zn**	0.05	0.019	0.036
3	**Mn**	0.05	0.02	0.03
4	**Ni**	0.05	0.009	0.012
5	**Pb**	0.05	0.009	0.038
6	**Fe**	0.05	0.007	0.03
7	**Mg**	0.05	0.0002	0.035

Both techniques had their limitations and drawbacks as well. The precipitation technique didn't cause 100% removal of metals because of the complexes formed by various metals and it was a time consuming technique as well. The efficiency of precipitation technique has a direct relation with the amount of metals present. The more the quantities of heavy metals more will be the efficiency of precipitation method. On the other hand, Biochar technique caused a slight change in color of the water.

After a complete cost benefit analysis, Biochar method has proved itself to be a more effective and efficient method in heavy metals removal as compared to the precipitation method. This technique should also be applied at industrial scale. Precipitation method isn't effective in the removal of metals which form complexes. It isn't feasible for the metals which are in traces. (Shim et al. 2014) worked on the efficiency of precipitation of heavy metals and found that precipitation only isn't enough for the removal of heavy metals and require the aid of other techniques.

For comparing the efficiency of both techniques, Single Factor Anova was applied and both techniques were compared individually. A summary of statistical analysis is given in this article. In table no.1 we can see that the P- value after Biochar treatment for Cu is 0.03. As the values of Cu were already very less therefore the P- value is not extremely less than 0.05. After precipitation treatment the P- value is 0.04 which shows that precipitation technique has done even less work in removing heavy metals than the Biochar technique.

P- value after Biochar technique = 0.03

P- value after precipitation technique = 0.04

As we can see that both values are less than 0.05 therefore we can say both have removed Cu but Biochar method was more efficient as it completely removed it. Same trend was followed for Zn and Mn. Ni, Pb and Fe are the metals which form complexes with hydroxides and increase their solubility. Precipitation method achieved only 50% removal efficiency whereas Biochar completely removed these metals. We can see in table 1 that the P –value of Biochar treatment for Ni is 0.009 whereas of precipitation treatment is 0.0129. As P – value of Biochar treatment is smaller than the P- value of precipitation treatment, therefore, we can say that Biochar treatment is more efficient in Ni removal. Same trend was followed for Fe and Pb.

Mg was detected in maximum quantity. Biochar managed to completely remove Mg

whereas precipitation only removed 75% of Mg. In table 1, we can also see that the P- value of Biochar for Mg is 0.00027 which is a very small value whereas for precipitation it is 0.03. As P-value of Biochar method is significantly smaller than 0.05, therefore, it can be concluded as a more effective method..

CONCLUSION

Biochar method proved to be a very efficient and effective method in heavy metals removal. It achieved 100% removal efficiency irrespective of the amount of metals whereas precipitation technique achieved only 75% removal efficiency. Biochar method was also a cheap method with great benefits whereas precipitation method was not cost effective. Blessed with the right kind of resources and an enabling environment, Pakistan has the potential to leverage the Biochar technology to rid it of some of its intractable problems. An appropriate investment at this stage in Research and Development is likely to accrue huge benefits in the foreseeable future.

CONFLICT OF INTEREST

The present study was performed in absence of any conflict of interest.

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AUTHOR CONTRIBUTIONS

SAC designed and performed the experiments and also wrote the manuscript. SRK provided supervision, technical assistance and reviewed the manuscript. All authors read and approved the final version.

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