Evaluation of Removal of TDS, COD and Heavy metals from Wastewater using Biochar

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***Abstract*- In this study, the adsorption capacity of Biochar has been investigated. The conventional treatment for heavy metal removal by chemical precipitation has problem of sludge generation. On the other hand, Adsorption of heavy metals using Biochar has no such problem.Sometimes activated carbon has been observed to be inefficient for the removalof TDS and Heavy metals, but biochar can effectively remove them. This technique can be used as a pre-treatment followed by biological treatment; so that TDS may be removed before biological treatment which enhances the efficiency of subsequent COD removal in biological treatment. From batch absorption experiments, it was observed that the removal was mainly through a surface precipitation using biochar. In batch adsorption study, variables like biochar dosage and contact time have been considered; at different biochar dosages and contact times, different removal efficiencies for TDS, COD and Heavy metals have been observed.The results for TDS, COD and Heavy metals removal from wastewater through adsorption using biochar shows overall good efficiency. The objective of this study is to utilize less expensive adsorbents for removal of TDS, COD and Heavy metals.**

***Index Terms*- Biochar, Adsorption, wastewater, Heavy metal**

I. INTRODUCTION

Biochar is one type of fine grained charcoal with high organic content. Biochar is a carbon-rich product which is generated through thermal decomposition of organic materials. It contains organic matter such as agriculture and wood waste, etc. Biochar is used as an adsorbent because of porous structure and large surface area. In India, much research has not been carried out in this area. In other countries, several studies have been done in which biochar is used as an adsorbent for removal of Heavy metals, TDS and COD by the batch or column experiments. Biochar adsorption characteristics depend on type of feedstock, process temperature and retention time.[1]

Biochar is a carbon-rich product generated through thermal decomposition of organic materials. Biochar has a strong affinity for organic compounds and has been increasingly investigated as an adsorbent for organic chemicals in wastewater and soils. Due to functional groups (acidity/basicity) biochar surface and π-π electron donor acceptor (EDA) interactions, toxic organic compounds can be sorbed by biochar.TDS is removed through biochar because of surface functional groups and high surface area.TDS is caused due to presence of sulphates, nitrates and chlorides in the dissolved form in the effluent. It is difficult to remove TDS. TDS is generally removed after secondary treatment by using advance wastewater treatments. Adsorption using biochar can be introduced as a pre-treatment for biological treatment; it gives effective removal of TDS before biological treatment [1]. The porous nature and surface chemical properties determine the adsorptive capabilities of biochar. Biochar may adsorb poly aromatic compounds, poly aromatic and poly aliphatic hydrocarbons, other toxic chemicals, metals and elements or pollutants in soils, sediments, aerosols and water bodies. The longer the time the more complete the adsorption will be. Surface area may increase with increase in peak temperature up to a certain critical or threshold value and then starts to decrease. It is also observed that biochar made at the lowest peak temperature has the lowest surface area (~10 m^2/ g), that produced at intermediate temperature (650–850°C) has the highest surface area (~400 m^2/ g); and that produced at temperature ≥1000 °C has the least surface area [3]. Heavy metal compounds are mostly soluble in the effluent, it effects on living beings in water stream and human beings also. Heavy metal adsorption through biochar is considered as surface complexion with carboxyl and hydroxyl groups and surface precipitation. [9].

Agriculture waste, wood waste, etc. are generally burned. Biochar can be produced from these waste materials; it is used as an adsorbent and it provides many other benefits to soil. So, Problem of burning is solved, It gives energy production in the form of syngas.

II. MATERIALS AND METHODS

2.1BIOCHAR

Biochar is produce by thermo-chemical decomposition of organic material at elevated temperature. Different methods for thermo-chemical conversion are available. Wet biomass is converted via Hydrothermal Carbonization (HTC) to biochar in water under high pressure and temperature around T = 200°C. Dry organic residues are more appropriate for pyrolysis or gasification systems working in a temperature range of T = 300°C to 800°C.It converts biomass into liquid, gas and high carbon, fine grained solid residue which is biochar.Three main factors influencing the properties of biochar are (Glaser et al. 2002a): i) the type of organic matter used for charring ii) the charring environment (e.g. temperature and type of atmosphere), and iii) additions during the charring process [5]. The type of feedstock strongly influences the elemental composition of the biochar, its accompanying ash, and porous structure and adsorption properties of the resulting activated carbons. Biochar is used as an adsorbent because of characteristics of porous structure and large surface area.There are different types of feedstock available like, agriculture waste, wood, baggasse, rice hulls, sludge derived biochar, dairy derived biochar and cow manure, bamboo waste, etc.

The adsorption of dissolved solids and heavy metal ions by low cost adsorbentswas evaluated under various conditions of pH, mixing speed, adsorbent doseand retention time.

Table1. At different temperature Biochar Production (From literature)

Process	Temperature & Duration	Solid (Biochar) (B)	Liquid (bio-oil)	Gas (syngas)
Slow pyrolysis	~500 oC, Days	35%	30%	35%
Fast pyrolysis	~500 oC, Sec.	12%	75%	13%
Gasification	>800 oC, Hours	10%	5%	85%

2.2 LITERATURE REVIEW: BATCH EXPERIMENTS

In a batch study,first the dose of adsorbent is determined.After that dose added to sample shaker for certain period of time with specific mixing speed and then it is used for determination of COD and TDS and heavy metal removal.Sample is first filtered and then analysed by the test.The metal quantity in solutions was determined by AAS before and after thesorption experiments. Here, experiment from literature explained method for TDS, COD and heavy metal removal.

Seok-Young Oh, Dong-Sik Shinconducted batch and column test both for TDS removal. From literature, it is found that the experiments were performed using 50ml of spent caustic and various amounts of biochar at 20±3ºC. The vials were shaken at 180rpm in a shaking water bath. After equilibrium was reached at 2h, the solution from each replicate flask was passed through a 0.22-mm cellulose membrane filter. In literature, batch experiments were performed for TDS and COD removal. The addition of biochar resulted in marketed removal of TDS from spent caustic. With 1 g of biochar, 17% of TDS was removed. Bichar amount increased, resulting 63% removal of TDS with 6g of biochar. The results indicate that approximately 0.19–0.30 g of TDS in spent caustic was removed by 1 g of biochar. However, a further increase of biochar to 10 g did not show additional removal of TDS from the spent caustic limited. In the column experiment, we observed the removal of spent caustic over various retention times [1].ManduInyan , Bin Gao, Ying Yao, Yingwen Xue, Andrew R. Zimmerman, Pratap Pullammanappallil, Xinde Cao; they were used the feedstock of dairy waste and sugar beet. The biochars made from the residue materials were first dried at 80ºC.Slow pyrolysis process about 500g of dried feedstock heated at 600ºC for 2h in a N_2 environment in a furnace. The concentration of each metal in the solution was adjusted to be 0.1mmol/L. There was 0.1g of biochar was added into 68mL digested vessels and mixed with 50mL of heavy metal solution at room temperature (22±0.5ºC).After shaking in a reciprocating shaker for 24h. The removal efficiency of the four metals

by DWSBS (digested whole sugar beet biochar) was higher than 97%.This biochar has a strong affinity for all the tested heavy metals. DAWC (digested dairy waste biochar) has showed high removal efficiency for Pb^{+2}(99%) and Cu^{+2}(98%),but low removal efficiency for Cd^{+2}(57%) and Ni^{+2}(26%)DAWC and DWSBS sorbents[2].PuskerRegmi, Jose Luis Garcia Moscoso, Sandeep Kumar, Xiaoyan Cao, Jingdong Maob, GarySchafran, First they made 50 mL aqueous copper or cadmium solution at temperature 23±1ºC for 24h. After 24 h, solutions were collected and filtered through a 0.45-mm nylon filter at regular intervals in glass tubes. Batch experiments were conducted with an initial metal concentration of 40 mg/L at pH 5.0 and contact time of 24 h resulted in close to 100% copper and cadmium removal by activated HTCB at 2 g/L, far greater than what was observed for HTC biochar (16% and 5.6%) and PAC (4% and 7.7%). The adsorption capacities of activated HTCB for cadmium removal were 34 mg/g and copper removal was 31 mg/g. The activated HTCB exhibited a higher adsorption potential for copper and cadmium than HTC biochar and PAC [3]. Hongmei Jin, Sergio Capareda, Zhizhou Chang, Jun Gao, YuedingXu, Jianying Zhang; they were used the feedstock of agriculture waste and fly ash. The metal concentration of 10 mg/l of (Cu, Ni, Fe) at an agitation rate of 200 rpm with an adsorbent time of 20 min at room temperature (25± 3).The Langmuir isotherms were obtained by equilibrating metal ion solutions of different adsorbent doses (5–30) mg/l with different times (20–150 min) at equilibrium pH and rpm with an initial metal concentration of 10 mg/l at room temperature. The removal efficiency for Fe, Pb, Ni were 99.25%,87.17%,96.15%respectively by rice husk and Cd, Cu were 73.54%,98.54% by fly ash. . The results of using real wastewater showed that rice husk was effective in the simultaneous removal of Fe, Pb and Ni whereas fly ash was effective in the removal of Cd and Cu [4].XiaoyunXu, Xinde Cao, Ling Zhao, Hailong Wang, Hongran Yu, Bin Gao, The experiment was conducted in 60mL polypropylene tubes by mixing 0.125g biochar with 25mL 0.01 M $NaNO_3$ solution containing 0,1,2,3,4 and 5mM Cu, Zn or Cd respectively. The mixture was then agitated on a reciprocating shaker at 100rpm for 10h.The time was shown enough for sorption of all metals to reach equilibrium, determined by preliminary experiment. After equilibrium, solid and liquid phases were separated by centrifugation at 4000rpm for 15min and the solution was filtered through a 0.22-µm Millipore filter. The metal concentration was determined by atomic adsorption spectroscopy (AAS). The maximum sorption capacities of Cu, Zn and Cd by DM200 were 48.4, 31.6 and 31.9mg/g, respectively and 54.4, 32.8 and 51.4mg/g by DM350 [5]Katarínaštefušová, Michal lovás, Anton zubrik, Marekmatik, Miroslavaváclavíková, All the experiments were conducted in batch. The initial Cd and Pb concentration was 10-200mg/L and 10-250 mg/L, respectively. The sorbent concentration was 2 g/L. The pH of the solutions was adjusted to value of 5.0 with 0.01 and 0.1 M NaOH and HNO3.The experiments were performed at constant temperature of 25°C in a rotary shaker set at 30 rpm and equilibrium time 24 hours. The metal quantity of solution was determined by AAS. The maximum sorption affinity of studied materials was observed in the case of rapeseed and its sorption capacity was 31.6 and 83.5 mg/g for Cd and Pb [8].

2.3 LITERATURE REVIEW COLUMN EXPERIMENTS

Seok-Young Oh, Dong-Sik Shin,wasconducted column experiment using a glass column (2.5cm(D)_22cm (L), packed with biochar toevaluate the removal of dissolved constituents from the spent causticin a continuous flow system. The column was packed with biochar(18 cm) and 2 cm of the column from each end was packed withquartz sand. Preliminary experiments confirmed that the removal ofTDS by the quartz sand was inefficient. The porosity of the biocharcolumn was 0.69. By changing the flow rate of a peristaltic pumphydraulic retention times (HRTs)in the columns were maintained differently at 7.0, 23.3, 36.2, and51.8 min, which were calculated based on the void volume of columnand flow rate. In order to compare the results of column experimentsunder identical conditions, a new biochar column was prepared foreach flow rate. After at least three times of HRT passed at each flowrate, column effluent was sampled and filtered through a 0.22-mmcellulose membrane filter to remove particles prior to TDS analysis [1].

2.4CALCULATIONS

The amount of the metal sorbed (mg) per unit mass of sorbents (g),q_{eq} was calculated using the Equation

$q_{eq}=\frac{Co-Ceq}{Cs}$

Where *Co*and *Ceq*are the initial and the equilibrium metal concentration (mg/L) respectively, and*Cs* is the sorbent concentration in solution (g/L).

III. LITERATURE RESULTS

These results are taken from literature for TDS and COD removal by the column experiment. From the result, it is found that whenretention time was increased, removal was also increased.Removal of COD and TDS in spent caustic using biological treatment with (i) no pre-treatment and (ii) after pre-treatment with biochar are compared, results are given in the following table.

Table2. Results (For TDS and COD removal) [Source: [1]]

Retention time (min)	Column experiments for TDS removal	Retention time (min)	Column experiments COD removal (Initial-8240mg/L)
7	34,000mg/L	23.3	1200-2300mg/L
36.2	25,000mg/L	51.8	700-1200mg/L
51.8	16,000mg/L	-	-

Table 3.Removal efficiencyof different biochar (for heavy metal removal)

Biochar	**Metals Removed**	**Dosing**	**Contact Time**	**pH**	**Removal efficiency**
Rice Husk[7]	Fe, Ni, Pb	20-60mg/l	20-120min	2-10	Fe-99.25% Pb-87.17% Ni-96.95%
Dairy manure [5]	Cu,Zn,Cd	5g/l	10hr for equilibrium	-	DM200:80-100% DM350:75-100%
Pine-needles[10]	uranium	2g/L	50min	6	99%
Dairy waste &Sugar beet[2]	Pb, Cu, Ni, Cd	2g/l	24hr	Dairy-10 Sugar-9	DAWC-Pb99%,Cu98, DASBC-97%

Table4. Adsorption capacity of different biochar (for heavy metal removal)

Biochar	**Removal**	**Dosing**	**Contact Time**	**pH**	**Adsorption capacity**
Switch Grass[3]	Cu,Cd	0.1-2g/l	24hr	2-10, pH-5	Cd-34mg/g Cu-31mg/g
Biochar residues[8]	Cd,Pb	2g/L	2hr	5	Cd-31.6mg/g Pb-83.5mg/g
Sludge derivedbiochar[9]	Pb	0.5-1g/l	10min	5	Pb-16mg/g

3.2Parameters that affect the biochar(data based on literature)

3.2.1 Effect of solution pH

The pH of solution is one of the most important parameters affecting adsorption through its effect on adsorbent surface charge and ionization and influencing the degree of ionization and speciation of the adsorbate. pH is a very important parameter. We have to analyze pH at which adsorption is maximum/optimum, It is called optimum pH.pH between 2-10 shows effective removal for heavy

metals. For TDS and COD removal, pH adjustment was not required (from the study).

3.2.2.Dose of adsorbent

First, we have to analyze at which dosing adsorption is high. Biochar dose was0.1-5g/L(data from the study) generally for heavy metal removal. Biochar dose was 120-190g/L for TDS removal.

3.2.3. Contact time for adsorbent

Adsorbent has provided certain mixing speed shaker for certain contact time.Contact times, were taken as hour and minute.Adsorbent was mixed with the solution at certain temperature(25ºC) and then shacked in reciprocating shaker equilibrium for 24h.When they increase contact time, effective removal occurred.

IV. CONCLUSION

The batch adsorption study shows the effects of varying the biochar dose and contact time on TDS, COD and heavy metalremoval efficiency from wastewater. The results for TDS, COD and heavy metal removal from wastewater are observed to have high efficiency. Optimum Biochar dose for heavy metal removal was 0.1-5g/L and for TDS and COD removal was 120-190g/L.Adsorbent is mixed at certain temperature (25ºC) then it is shacked in reciprocating shaker equilibrium for 24h. Adsorbent is mixed at certain rpm for certain hours or minutes. From the study, it can be concluded that biochar is a less expensive adsorbent which can be usedfor removal of TDS, COD and Heavy metals.

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