PREPARATION OF ACTIVATED BIOCHAR AND ITS USE IN ELIMINATION OF CHROMIUM FROM SELF-CONTAMINATED AQUEOUS SOLUTION

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Dedicated to my worthy parents, and siblings whose tremendous support and cooperation led me to this wonderful accomplishment

I Also dedicate it to my in-laws, most importantly my spouse, mother-in-law & father-in-law and brother for breaking traditional stereotype thinking and supporting me out of the way.

May Allah grant me the strength and ability to live up to their expectations.

Ameen

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ABSTRACT

Unprocessed industrial chemicals dumping in lakes and rivers possess a severe environmental risk through metals pollution within the food chain, especially Chromium. As Chromium is carcinogenic in nature, but it is present beyond permissible limit in less developing countries. It needs to be removed at least from drinking water. Iron modification has been extensively used for metal removal This work uses solid green waste for removing heavy metal Cr (VI). Mainly focuses upon the use of $FeCl_3$ modified biochar utilizing sugarcane bagasse and peanut shell powder as biomass for Cr(VI) removal from self-contaminated water. Adsorbent was prepared using Bench-Scale Fixed Bed Reactor (B-SFBR) and Cr (VI) determination colorimetric method was applied. Adsorbent was examined by different analytical techniques. Thermogravimetric (TGA) was done for checking degradation temperature of biomass. A decrease in BET surface area was observed as from 53.2132 m²/g to 10.0048 m²/g for raw and $FeCl_3$ modified PSP and from 49.6679 m²/g to 18.5476 for raw and $FeCl_3$ modified SBP by Brunauer-Emmett-Teller analysis, smaller surface area is the result of iron modification. Morphological structure and elemental analysis were done by SEM-EDX and attached functional groups by FTIR spectroscopy. Coherency in data was checked by pseudo 1st and 2nd order kinetics model. Batch experimental study was done by observing variation of time by fixing other parameters. Highest removal was achieved by Modified Peanut shell Powder with 99.97% removal upon pH = 2, shaking time = 180 mints, shaking speed = 150 rpm, absorbent dose of 0.3 g, Cr (VI) conc = 20 mg/L. Removal of Cr (VI) using Modified Sugarcane Bagasse was 98.96% with Cr (VI) conc = 20 mg/L, absorbent dosage = 0.3 g, pH = 2, shaking speed = 150 rpm, shaking time = 180 mints. It was acknowledged from present experimental research that, $FeCl_3$ modified peanut shell powder shows greater Cr (VI) removal efficiency as off sugarcane bagasse.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBRIVATIONS

IARC	International Agency for Research on Cancer
USEPA	United State Environmental Protection Agency
KPK	Khyber Pakhtunkhwa
ITE	Industrial Trading Estate
PSP	Peanut Shell Powder
SBP	Sugarcane Bagasse Powder
PID	Proportional-Integral-Derivative
FeCl$_3$	Ferric Chloride
B-SFBR	Bench-Scale Fixed Bed Reactor
Cr (VI)	Chromium having oxidation state +6
AC	Activated Carbon
FeCl$_3$-PSP	Ferric Chloride activated Peanut Shell Powder
FeCl$_3$-SBP	Ferric Chloride activated Sugarcane Bagasse Powder
TGA	Thermo-Gravimetric Analysis
SC	Standard Calibration
DPC	1,5-diphnylcarbazide

CHAPTER   1

1   INTRODUCTION

1.1   Adsorption

As urbanization is increasing, water pollution goes on increase and availability of clean and safe drinking water becoming very less (Sultana et al., 2022). Pollution in water is increasing day by day because of industrial revolution. From last several years use of adsorption process for the removal of heavy metals and purification of water is being used. The most commonly and economical and low-cost method for the removing metals from water is done by using biochar as adsorbent. Every low-cost waste having high percentage of carbon compounds can be used adsorbent for making activated carbon (Bansal, 1988). Adsorption basically attribute to attachment of molecules onto another surface. Some solids can stick or adsorb different substances from any solution onto them. This is largely used in different industrial units to purify heavy metals, bad odors, and different impurities from water and to make it free from any impurities. The medium used to remove impurities called as adsorbent and material or particles which adsorb can be refer as adsorbate. There are largely two main classifications of adsorbent subjecting to involved forces, chemisorption and adsorbate-physisorption (Of & Carbon, 2012).

1.2   Chromium Pollution

Stable oxidation of Cr in water are only two, Cr (III) and Cr (VI). Cr (III) is very critical for the nutrition of human for the digestion of glucose, it become very dangerous when concentration is high above >150 mg L^{-1} for the physiology of plant (Nematshahi et al., 2012). As chromium is carcinogenic in nature, it contributes to decrease or increase mutagens inside human body. Less developed, poor, or developing countries suffer from this ailment comparatively more than that of rich and developed countries. Health risks linked or attached with heavy meatal and especially with chromium must be strictly implemented with international regulations. Cr^{+6} is 1000 times more toxic as compared to Cr^{+3}. Chromium vigorously effect respiratory organs, ulcer formation, skin, nasal septum, liver disorders, bronchitis infection (Miretzky & Cirelli, 2010) (Parlayici & Pehlivan, 2019) (Zhang et al., 2004) (Mutongo et al., 2014) (L. N. Rao et al., 2011). USEPA and WHO recommended the concentration of chromium in drinking water must be low that 50µg/L. in Pakistan chromium concentration is very high owing release of water from textile, leather, metal finishing, cement, fabrication industry, electroplating, tanning industries releases 0.5-270

mg/L concentration of chromium in water. (Cronje et al., 2011) (Ghosh, 2009) (Solangi et al., 2020). Diagrammatic view is shown in Fig 1.1 as under.
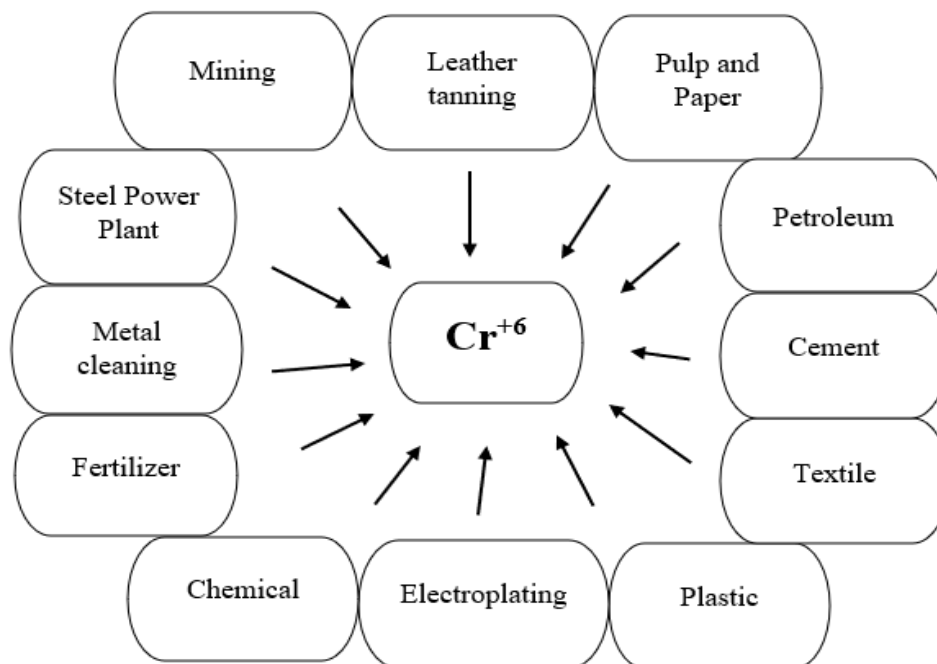
Figure 1.1 Industrial sources which lead to Cr^{+6} pollution (Haroon, 2016)**.**

Cr (VI) present even at 0.05 mg/L concentration inside natural water is very carcinogenic. (Sarkar et al., 2010). Cr (VI) when get attached oxygen it forms dichromate and chromate. These both are strongly water soluble and is less adsorbed in soil as compared to water and leads to water contamination and pollution (Dittert et al., 2014).

Cr (VI) when present in acidic medium it forms dichromate and chromate anions with hydrogen, whereas it forms chromate anions in basic media (Barnhart, 1997) (Najim et al., 2014). Moreover, Cr (VI) has great oxidizing power and fast mobility that is why it is bioavailable inside the body for 39 hours (Kerger et al., 1996). In biological system it can behave as teratogen, mutagenic and a carcinogenic element (Gómez & Callao, 2006). As Cr (VI) is highly soluble in water that is why it can easily penetrate from the skin and get mix in blood stream and can easy cause gastric or liver damage, kidney and lung cancer, skin irritation and many other health problems. Toxicity of Cr (VI) exists 100 times more than Cr (III) whereas cytotoxicity and mutagenicity of Cr (VI) is approximately 1000 times than of Cr (III). Whereas toxicity of Cr (VI) is linked with formation of free radical and oxidizing power within cell during the reduction of Cr (VI) to (III) (Egli et al., 2003).

In list of unsafe and hazardous materials Cr (VI) is placed in the top most place because of its carcinogenic and mutagenic modifications inside living tissues (Moussavi & Barikbin, 2010). Owing to its toxic nature United State Environmental Protection Agency categorizes it to inhalation carcinogen as in Group A and IARC categorizes it in human carcinogen as top in Group I (Sreenivas et al., 2014). USEPA gives limit of about 0.05 mg/L of Cr for portable water whereas conc of 0.1 mg/L is for landfill discharge. (Geleel et al., 2013). Movie of Hollywood blockbuster, Erin Brockovitch showed the toxicity of Cr(VI) (P. Saha, 2010). Among industries wastewater coming from tanneries majorly contributes to Cr(VI) pollution when released untreated into lakes and rivers. In sub-continent region tanning industries contains 2000-5000 mg/L out of which they releases about 2000-3000 tons annually untreated in environment (Belay, 2010). About 90% industries in Bangladesh uses simple way of chrome tanning which gives good results to leather. Tanning is actually wet process which need large amount of water and releases 90% effluent (Chowdhury et al., 2013). Some Researchers from Bangladesh finds that skin diseases (31%), gastrointestinal disease (58%), hypertension (12%) and jaundice (19%) results in ingestion of Cr in living body. An investigation was conducted in Nepal on district Bara and Parsa and results shows 345mg/L of Cr concentration only in sample taken from Leather Production (Dhungana & Yadav, 1970).

1.3 Chromium pollution in Ground and Surface water of Pakistan

Unprocessed industrial wastewater dispenses out in streams in Pakistan. The maximum allowed limit for industrial effluents Cr(VI) is 0.1 mg/L. Nevertheless 0.05 mg/L concentration of Cr(VI) is for drinking water (Haroon, 2016) (R. Saha et al., 2011) (Sreenivas et al., 2014). Similarly 0.05 mg/L is limit as according to PAK EPA too (S. Khan et al., 2013). So, it is compulsory for every country to do no cross the permissible limit provided and to treat the waste as needed before dumping or releasing it in water. Much research has shown high amount of chromium concentration in wastewaters.

In Pakistan there are many unregistered and registered tanneries and footwear making units (Ahmed et al., 2016). As reported in research in Pakistan 650 registered tannery, out of these 264 are in Sialkot which release 144502.1-215036.1 gallons of wastewater in all chrome tanning process (Qadir et al., 2008). When these wastewater from gallons is analyzed results shown a high amount of chromium concentration about 592 mg/L (Zvinowanda et al., 2009). In 2011 Karachi-Korangi chromium concentration in residue and filtrate wastewater have 18.75-170.12

mg/L and 15.2-185.5 mg/L (Parveen et al., 2013).

In district Kasur, water contamination by chromium is 90 mg/L. Whereas water from monitoring wells have chromium of about 10.4 mg/L. industrial wastewater of Kasur have a concentration of 68 mg/L-2,152 mg/L. this concentration can be easily seep into soil(Pandey et al., 2018). A research has been done on 15 industrial wastewater and results shows 25.93 mg/L of chromium concentration which is far beyond that permissible limit (Ahmed et al., 2016). In Nowshera KPK chromium concentration in surface water was 0.16-0.29 mg/L (Nazif et al., 2006). Well water of Kasur and wastewater from industries in Peshawar have chromium concentration 51.70 mg/L and 2.12 mg/L (Tariq et al., 2008) (Tariq et al., 2006). In Karachi, Landhi, Korangi have 0.82 mg/L of Cr and water coming in tap have 0.082 mg/L (Kishore et al., 2013). China has limit of 0.05 mg/L for surface water and 0.5 mg/L for wastewater. They strictly monitor and regulate this concentration (Lyu et al., 2017).

Groundwater of Sialkot have 0.0-0.30 mg/L of chromium concentration (Ahmed et al., 2016). In Sahiwal drinking water have 5.498 mg/L of chromium concentration (Haroon, 2016). Moreover, only one sample out of twelve have high-level concentration of Cr about 0.6 mg/L from Sheikhupura (Gilani et al., 2013). These high concentration shows that industries do not treat water before they release their effluent into water in Pakistan and they do not act upon Environmental Law.

1.4   Cr (VI) Treatment

Various methods are reported for isolation of metals from industrial wastewater including ion exchange (Yuan et al., 2008)(Kim et al., 2008)(Yu et al., 2014), microfiltration, ultra-filtration, membrane filtration(Qadir et al., 2008), reverse osmosis, cementation, electrocoagulation, solvent extraction, by using commercially made activated carbon, chemical precipitation, (Akar et al., 2009) (Nadeem et al., 2006) (Nadeem et al., 2006) (Quintelas et al., 2009) (Sari & Tuzen, 2008)(Suresh et al., 2011) (Akmar Zakaria et al., 2009) reduction of various adsorbent onto another adsorbents (Erdem et al., 2004)(Monser & Adhoum, 2002). These all methods of removal of heavy metals are not economical for developing or underdeveloped countries. Majorly these methods are efficient for specifically of concentration 1-100mg/L in a solution (Guo et al., 2019). They need high capital investment, maintenance cost, huge amount of land and fuel consumption for transportation. Collectively it possesses many disadvantages on economy, health sector, environment, and many other phases of country. So, these methods are

quite inefficient and less effective for the countries like Pakistan and many other (Kishore et al., 2013). Hence, those methods are needed to apply which requires naturally large available resources.

BC is a useful adsorbent to remove heavy metal like Cr(VI) owing to its good specific surface area and stable porous size. It is carbon-rich strong material of any bio-waste and is typically prepared by pyrolysis process of biomass under slightly higher temperature and oxygen-limited environment, inert environment. It can be generated from various biomaterials (such as wood, animal manure, agricultural residues, and sludge and plant by-products (coconut shells, corn-bran, water hyacinths). The larger surface area, efficient functional groups, high porosity of BC which makes it an outstanding adsorbent for removal of Cr(VI) from soil and aqueous solutions.

Various adsorbents are used for removal of Cr(VI) i.e., zeolites (Yusof & Malek, 2009), silica (W. Liu et al., 2010), biochar (Pan et al., 2014), carbon fiber (Miretzky & Cirelli, 2010), and activated carbon (L. N. Rao et al., 2011), etc.

Readymade activated carbon imported from different developed countries collective become so expensive as to treat all the drinking water to feed all people and to meet household or industrial needs. It is very tough for countries like us to deal with clean and safe drinking water. The major requirement is that we need to make adsorbents from generated wastes, which have large adsorption capacities. It is new and fresh emerging field of research (Oboh et al., 2009). Alongside of availability, cost effectiveness, seasonality and location, from literature it can be seen that there are many advantages of adsorbents having low costs as those commercial ways to treat heavy metals from the effluents(Gardea-Torresdey et al., 2004). The ascendency include greater efficiency, less formation of sludge, economical, rehabilitation of adsorbents by recovery of metal (Sud et al., 2008). More benefits for industries which discharge pre-treated waste water and corporate with environmental responsibilities(Basumatary et al., 2016). Literature confirms that this is now growing and emerging field for clean and safe drinking water to feed the upgrowing population(Gupta et al., 2009)(Odoemelam et al., 2011)(Opeolu et al., 2009)(Haroon, 2016).

1.5   literature Review

There are vast number of plants and agricultural waste available. Literature confirms about the use of waste as adsorbents (Agarwal et al., 2006). Chemical composition of waste is factor which can be under observation while successful metal uptake(Haroon, 2016). Lignocellulosic

biomasses have both cellulose and lignin, which are important factors for removal of any heavy metal from water. Cellulosic material found as an fairly good adsorbent for the removal of heavy metals (Opeolu et al., 2010). Carboxylic and phenolic groups present on exterior of agricultural material makes it good adsorbent for removal of metal (Castro et al., 2011). Peels of banana and other agricultural waste can be successfully used as adsorbent for metal removal (Harman et al., 2007). Active site of adsorbent is responsible for adsorption it includes amine (NH_2), hydroxyl (OH), carboxyl (COO), amide ($RC(O)NH_2$), or carbonyl (CO). Polar groups also attached like carboxylate (RCOO), ethers (R-O-R), aldehydes (RCOR), alcohols (R-OH), ketones (RCOR), phenols (C_6H_5-OH), they combine with metal ions and make a complex with detaching H^+ or H^- ion or an electron pair (Ofomaja & Ho, 2007). These kinds of adsorbents are used for extracting or engulfing heavy metals from wastewater or any polluted water (Mousavi & Seyedi, 2011)(Haroon, 2016)(Haroon, 2016). Despite every commercially available adsorbent natural adsorbent i.e., which are made by using green waste like walnut sawdust activated or non-activated (Y Bulut & Tez, 2003), residue or discard of tea industry, wheat bran(Yasemin Bulut & Baysal, 2006), sugarcane bagasse (Haroon, 2016), leaves (Haroon, 2016), cotton seeds (Srinivasan & Sathiya, 2009), rice hull (L. H. Wang & Lin, 2008), pomegranate peel (Haroon, 2016), tea leaves (Kishore et al., 2013), saw dust (Yasemin & Zeki, 2007), cereal crops (Miretzky & Cirelli, 2010), banana peels (Castro et al., 2011) are good availability, high efficient and is very economical. Commodity crops like sugarcane bagasse, tree waste, peanut shell, or other dry agricultural waste produced in large quantities and have very less importance generally in poor and underdeveloped or developing countries like Pakistan. Specifically peanut shells are less in weight but large and seldomly used as animal feed or can be burned to reduce space. World`s largest peanut producer is China and have a potential of producing 4.5 million tons peanut (Tao & Xiaoqin, 2008). North Carolina is fourth biggest producer with 95.2000 metric tons of it like 6.3% of US production. These values show 26000 metric tons of peanut shell produced have very little value if left untreated. This huge waste needed to be converted as useful way by converting it to activated carbon and used as an adsorbent for removal of heavy or light metal ions and other impurities and organic compounds. (Namasivayam & Periasamy, 1993)(Periasamy & Namasivayam, 1995a)(Periasamy & Namasivayam, 1995b)(Periasamy & Namasivayam, 1996)(AL-Othman et al., 2012).

Various biological, physical and chemical methods are used for removal of heavy metals from

aqueous solution or wastewater (R. A. K. Rao & Rehman, 2010). They include biological operations (Sivakumar, 2013), ultrafiltration(R. A. K. Rao & Rehman, 2010), ion exchange(L.-C. Lin et al., 2008), chemical precipitation, microfiltration, electrodialysis and reverse osmosis (Barrera-Díaz et al., 2012).

1.6   Methods for removal of Cr(VI)

1.6.1   Chemical Precipitation

It is most effective and common method for treatment of heavy metals (Kurniawan et al., 2006). This process make soluble salts or impurities to insoluble ones by using a precipitating agent and results in speedup of a chemical reaction (Barbooti et al., 2008). Sodium bicarbonate, lime or caustic soda commonly worn as activating agent. Nevertheless, removal of Cr (VI) is impossible by this method as it is high soluble and in solution precipitation process does not start on any pH (Anderson, 1989). Generally, Cr (VI) removal is two-step process: firstly, reduction of Cr(VI) to Cr (III) happens; secondly Cr (III) precipitates out. Reducing agents like sodium bisulphite ($NaHSO_3$), sodium metabisulphite ($Na_2S_2O_5$), ferrous sulphate and sulphur dioxide (SO_2) (Nriagu & Nieboer, 1988) (C. J. J. Lin & Vesilind, 1995).

This process has some limitation as it utilizes bases and acid, liberation of harmful gas i.e., H_2S, production of sludge and sludge disposal (Nriagu & Nieboer, 1988). It is not an economical process. Moreover, it is more time-consuming process which prompt into precipitates aggregation (Akbal & Camcı, 2012)(Kurniawan et al., 2006)(Mohan & Pittman Jr, 2006)(Mohan et al., 2011).

1.6.2   Ion Exchange

This is a suitable method for decontamination of noxious metals like Cr (VI) (Rivero et al., 2004). There are many materials used in ion exchange method for removal of Cr(VI) below 0.05 mg L^{-1} from wastewater. Ion exchanger (solid) are those materials which can exchange cations or anions from surroundings. Normally there are synthetic ion exchangers like organic ones. For treatment of effluents (strongly basic) anionic exchangers are used like AV-17(Cl), have $N+(CH_3)_3$ groups, Varion AD which have $-N+(CH_3)_2C_2H_4OH$ stated as well-organized ion exchange (Drutsa et al., 2006). For treatment of wastewater resins of cationic ion-exchangers are used. At Cr(VI) concentration of 0.1 mg/L, pH= 5.8, with uptake capacity of 200 mg/g with dosage of 10 mg/100 mL (Rengaraj et al., 2003). By using this process waste reduces a lot. But process efficiency depends upon pH of water which is a main process drawback.

1.6.3 Solvent Extraction

Process of solvent extraction requires many associated system like tetraphenylstibonium, ammonium triphenylsulfonium, triphenylselenium cations and triphenylphosphonium (Venkateswaran & Palanivelu, 2004). For removal of chromium solvents like ethyl acetate, tri-n-butylphosphate, diethyl ether, chloroform, and isobutyl ketone are reported in literature (Venkateswaran & Palanivelu, 2004). NaCl, NaNO₃, NaSO₃, NaOH used as strip paints for Cr(VI) removal (Venkateswaran & Palanivelu, 2004). Its major drawback is removal of wastewater and loss of solvent.

1.6.4   Membrane Separation

Membrane technology is widely used in chemical and environmental engineering for desalination and treatment of wastewater. There are four different pressure-driven techniques i.e., reverse osmosis (RO), ultrafiltration (UF), nanofiltration (NF) and microfiltration.

NF and RO are most suitable techniques by which metals can be removed in form of ions. This method does not need any extra chemical. Cr(VI) can be managed by membranes of MPS-34 (NF) and NF90 (NF) and BW30 (RO). BW30 (RO) and MPS-34 (NF) show removal >97% whereas NF90 shows 99.5% removal (Piedra et al., 2015).

The membrane of ultrafiltration has cellulose acetate, polyethylene glycol and nanochitosan with ratio 1:2:2 can be used for Cr(VI) removal. Literature shows that thickness having 0.2, at pH 7, with pressure 100 kPa can remove Cr(VI) 95.64 % (Vinodhini & Sudha, 2017). Another membrane on pH > 7, with Cr concentration of < 25 mg/L, literature shows by this > 90 % of Cr(VI) can be removed (Piedra et al., 2015).

1.6.5 Foam Separation

It is economical technique and is a surface adsorption phenomenon. Adsorption occurs interface of gas-liquid among dispersed phase and liquid phase. This method involves non-active or active materials of surface through adsorption with surfactants. This can remove Chromium up to 97.80 % with pH of 4, 0.9 L min^{-1} air flow, 300 mg/L of surfactant dosage and initial concentration of 10 mg/L (Jiao & Ding, 2009).

1.6.6 Reduction

Reduction involves the conversion of high to lower oxidation state of metallic ions (Martinez & Rodriguez, 2007). In case of chromium metal Cr(VI) is reduced to Cr(III) which is less toxic, but it does not remove chromium completely from solution. If reduction can used with the process of

sorption, ion exchange and coagulation it can be more effective. It can be done by methods like electro-catalytic, electrochemical, and chemical reduction (Salimi et al., 2006). Chemical reduction uses reducing agents as hydrogen thiols, sulfide, hydrogen, and iron peroxide. Literature shows the use of bacteria for reduction of Cr(VI) (Wielinga et al., 2001).

Process of electrochemical reduction is an alternative method for chemical reduction. This is basically electrochemical reduction, as electric current is given by chemical reduction. It has an advantage of metal recovery and is a less time-consuming process (Hatfield et al., 1996)(Rajeshwar et al., 1994). Its main limitation, less economical, it need additional chemical and huge amount of hazardous sludge is produced and big advanced infrastructure is required for this to be implemented. This reduction process uses different electrodes made up of variety of materials. Among them electrode made by carbon steel is low cost and is efficient. From literature we come to know by using electrochemical technique, wastewater holding 1000 mg/L Cr(VI) for 38.5 min at pH 1 can be treated (Barriada et al., 2009).

1.6.7 Adsorption

An Adsorption is highly efficient, inexpensive, and simple method for wastewater therapy and is significantly inspired by formation of the adsorbate with side sound structure of the adsorbent. The external harmony of adsorbent material also provides uptake power of adsorptive also in adsorbable elimination system. This technique is effective and has ability to be cost-effective. The main benefits of the adsorption are the concurrent elimination of one or many ions present day in the effluent. These particles are adsorbed on top of solid permeable side and can be defined individually and quantitatively.

Farming plant residue have been utilized as adsorbents since they are simply and plentifully available, conservation friendly, cheap and have superior adsorption assets owing to their various physical and organic nature. Four methods, i.e., cationic adsorption, anionic adsorption, , cationic and anionic adsorption as well as adsorption-connected decrease are getting involvement in the therapy of chromium with different biomasses. Efforts have remained put together to discover heavy metallic adsorption of some low-cost and amply available natural wastes. Natural wastes provide high productivity, produce fewer slurry, and have restoration ability. Different operational groups like amine, carboxyl, carbonyl, amide, and hydroxyl on the side of these adsorbents make them a perfect choice as steel binding places.

1.6.8   Activation

In adsorption, (activated carbon) AC is described as the highly frequently used traditional adsorbent. Agrarian waste comprising lignin as well as celluloses fabrics that could be the probable choice and economical source for production of AC, since of its abundance, commercial viability, and renewability. Agrarian trash also reveals excellent properties like small amount of inanimate material, the existence of inanimate materials in both precursor raw material effects the adsorption capability of the subsequent activated adsorbents. Superior volatile substances, i.e., above 50%, help during carbonization in establishment of basic hole structure. Formation of AC from carbon-based materials contain two steps: first, formation of biochar in unreactive and pure atmosphere, which increases produced carbon contents, then also assistances in formation of early absorbency of the substantial; the additional step involves the activation of biochar, which helps to upsurge the total pore size. Nevertheless, activation process could also be achieved across chemical or physical methods.

In physical activation process, formation of biochar carried in an inert atmosphere commonly nitrogen gas is used because of its easy availability and low expense, tracked by activation using oxidizing agents, CO_2 or steam. In the development of chemical activation, forerunner material is initially infused with different chemicals like $ZnCl_2$, $FeCl_3$, H_3PO_4, NaOH, $AlCl_3$, or KOH and later carbonized into the manifestation of inert ambience. Between different chemical mediators, H_3PO_4 and $FeCl_3$ is the most applied infusing agent owing to its financial and environmental interest.

Chemical activation is additionally more economical and is desired to the basic method, as it requires decrease temperature for formation of biochar with fewer period for activation. Moreover, chemical activation causes in the structure of mesoporous AC with larger side area Other activating agents have some drawbacks like corrosion, unproductive recovery and the AC prepared by means of these elements cannot be rummage-sale in some diligences (pharmaceutical industries and food) as they might affect the cleanliness of mass-produced resources (Prahas et al., 2008).

1.7 Production methods for Biochar

The growing interest in using biochar for different treatments has led to expanded transformation of waste biomass into useful biochar. Thermochemical conversion is a conventional method for production of biochar. Thermochemical conversion method includes pyrolysis, gasification, hydrothermal carbonization (Pang, 2019)(Pang Z et al., 2020). For maximum biochar yield, the

choice of method depends upon temperature of area, mass availability, residence time should be optimum. These are important parameters which must be taken in consideration before choosing any technique of thermochemical conversion of waste.

1.7.1 Pyrolysis

This process for thermal decomposition of waste into useable matter occurs in the absence of oxygen with temperature range of 250 – 900°C called as pyrolysis (Osayi et al., 2014). This method is an alternative strategy for transforming the trash biomass into worth-added goods like biochar, bio-oil, and syngas. Throughout the procedure, lignocellulosic components like cellulose, lignin and hemicellulose undergo response processes like cross-linking, depolymerization and fragmentation at certain temperatures following another state of matter like solid, gas and liquid. The liquid and solid products containing bio-oil and char and gaseous products are CO_2, CO and hydrogen and syngas (C1-C2 hydrocarbons). Several kinds of reactors like bubbling fluidized bed, paddle kiln, wagon reactors, bed reactors and rotating kilns are normally used for production of biochar. Yield of biochar during pyrolysis process varies with nature and type of biomass used. Likewise Temperature is major operating parameter that decides efficiency of product (Wei et al., 2019). Generally, yield decreases, and formation of syngas increases with increase in temperature during pyrolysis process. The mechanism of the pyrolysis process is shown in Figure 1.2.
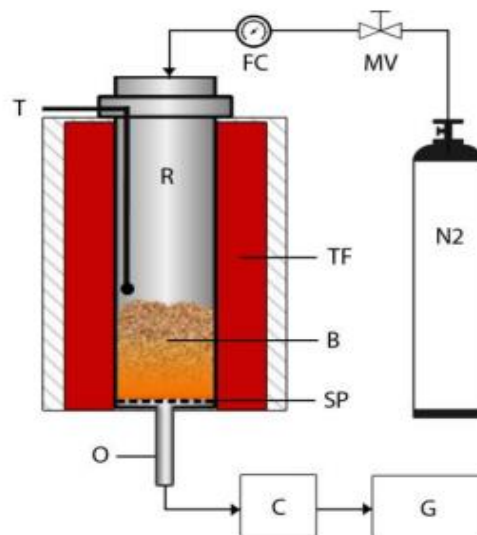

Figure 1.2 Schematic diagram of B-SFBR: FC = flow controller, MV = manual valve, N_2 = Nitrogen gas cylinder, T = thermocouple, R = fixed-bed reactor, TF = tubular furnace, B = biomass, SP = sieve plate, O = outlet, C = condenser, G = gas collector.

11

There are two categories of pyrolysis process 1. Fast pyrolysis 2. Slow pyrolysis. Fast pyrolysis is reflected as an immediate thermochemical method which can make slurry of solid biomass to bio-oil (liquid) with huge energy application. Its conditions: (i) short times for fumes and small biomass particles size and pyrolysis fumes (0.5–2 s) (ii) fast warming strides of biomass particles (>100 C/min), (iii) moderate treatment temperatures (400-600 ℃). A key characteristic factor of fast pyrolysis revolution is the necessary to maintain the fume habitation time in hot area to the base, to achieve good quality of bio-oil. This can be done by ensuring fast smothering or cooling the fumes (Y. Wang et al., 2014). Slow pyrolysis: In this pyrolysis, the rate of heating up is very less about 5-7 ℃/min and has a slower dwelling time of less than 1 h (W.-J. Liu et al., 2015). Slow pyrolysis invention has a well yield of char as compared with different pyrolysis or carbonization strategies. Biochar can also be utilized as a soil enhancer to improve its quality (Al Arni, 2018).

1.8   Justification of Study

After literature study, it is noticed that huge amount of work has been done already regarding removal of heavy metals from solution of wastewater, but the gap is comparative assessment between biomasses. For underdeveloped or developing countries like Pakistan which have excess of bio waste, dumped openly and people do not have excess of clean drinking water.

Therefore, it aims to highlight use of agricultural waste in an efficient purpose.

1.9   Objectives:

1. Preparation of efficient adsorbent (modified biochar) made from locally available biomass present in huge amount and its use for removal of Cr(VI) from the aqueous solution.

2. Analyze the Effect of time for removal of Cr(VI) using Modified biochar made from sugarcane bagasse or peanut shell.

CHAPTER 2

MATERIALS AND METHODS

2.1 Chemicals, instruments and Glassware used in Experiment

1,5-diphenylcarbazide ($C_{13}H_{14}N_4O$), acetone (CH_3COCH_3), ferric trichloride ($FeCl_3$), potassium dichromate ($K_2Cr_2O_7$), phosphoric acid (H_3PO_4), sulphuric acid (H_2SO_4) and hydrochloric acid (HCl) was purchased from Sohail Chemical Rawalpindi of company Sigma-Aldrich.

250 mL Erlenmeyer flask, 100 mL graduated cylinder, glass funnels, 50, 100, 500, 1000 mL volumetric flask, 10 mL glass pipets, 0.1 mL micro pipets, pestle and mortar, 500 mL washing bottle, 250 mL evaporating dish, watch glass, porcelain crucible and cover, cloth for efficient removal of iron during activation, droppers, and spatulas, this all glassware were used in this experiment.

2.2 Formation of 1,5-diphenylcarbazide Solution

The solution was prepared by dissolving concentration of 250 mg 1,5-diphenylcarbazide in 50 ml acetone in 50 mL volumetric flask having.

2.3 Adsorbent Preparation / Handling

Following are the steps for adsorbent preparation and batch experimentation (figure 2.1).
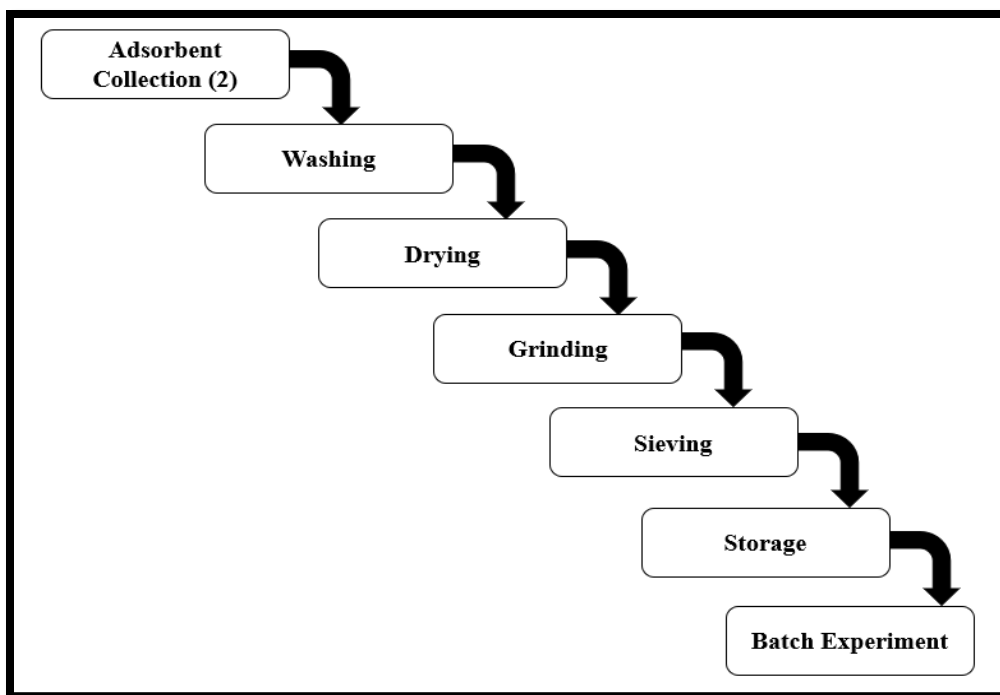
Figure 2.1 Adsorbent Preparation

2.3.1 Biomass Collection

Two agricultural waste (biomasses), *Saccharum officinarum* (sugarcane bagasse) collected from local market of Wah Cantt, Taxila Pakistan. *Arachis hypogaea shells* (peanut shell) was collected from Chakwal district, Pakistan.

Table 3.1 Biomasses Used

Sr No	Binomial Name	Common name	Shell/Tree	Urdu name
1.	Arachis hypogaea	Peanut	Shells	Mong Phali
2.	Saccharum officinarum	Sugarcane	Stalks	Ganna

2.3.2 Washing

Both biomasses were deeply washed twice with DI water for removal of debris, adhering material or dust particles.

2.3.3 Drying

Washed peanut shells and sugarcane bagasse were oven dried at 110℃ for 3 hours in heating oven.

2.3.4 Crushing and Straining

Both dried biomasses had been crushed using mechanical grinder (available in Biotechnology

14

Lab, NUST) and sieved by strainer having particle size of 1 mm – 1.41 mm. Leftover big particle size biomasses were then crushed using pastor and mortar first and then strain with 1 mm sieve.

2.3.5 Storage

Lastly, raw biomasses were then transferred to zip lock bags mentioned as adsorbent in present study.

2.4 Preparation of Biochar using Bench-Scale Fixed Bed Reactor (B-SFBR)

Pyrolysis was executed in a stainless-steel B-SFBR having internal diameter of 10.8 cm and length of 50.4 cm. Fiber insulated with ceramic was draped all over reactor for good temperature control which is optimum for pyrolysis process. To control direct heat reached to biomass from metal surface, a tough mica (silica-based) was used at the bottom of insulated blanket. Mica sheets have an advantage of long lifetime of insulating material having efficient and better temperature management. Ice-bath and solution of NaCl were used to decrease and lowers the temperature of condenser. Furthermore, to collect bio-oil and to check the flow of nitrogen gas 250 mL Erlenmeyer flask was used, which has rubber stopper to avoid release of bio-oil in working area. For the control of reactor temperature and to regulate heating rate PID controller were used. Pressure of 0.6 Psi were used at the start for nitrogen purging. After purging pressure were reduced to 0.1 Psi at all the time of making biochar.

For each batch test, 100 g sample was put into the reactor's core before the start of the experiment through top flange of reactor. Thereafter, reactor was airtight, and leakage was tested through bubble test. Formerly heating, reactor flooded with N_2 gas at the stream rate of 500 cm^3/min. for 30 min to make sure anoxic in the interior atmosphere to prevent combustion of sample. This procedure was also adopted by (S. R. Khan et al., 2021) The pyrolysis reactor (shown in Figure 2.4) was heat up to prearranged temperature of 550 °C complete Thermo-Gravimetric Analysis (TGA) experiment with heating rate of 50 °C/min. As the current study investigates pyrolysis of PSP and SBP (having high thermal strength) and end product is biochar shown in figure 2.2 and 2.3.

Figure 2.2 (A) Raw Sugarcane Bagasse (SB), (B) SB Powder (C) SB after pyrolysis

Figure 2.3 (A) Raw Peanut shell (PS), (B) PS Powder (C) PsS after pyrolysis

Figure 2.4 (A) Bench Scale Fixed Bed Reactor, (B) N_2 cylinder

2.5   Biochar Modification

At present, several methods have been developed to modify BC to enhance its adsorption of heavy metal oxyanions. Moreover, polyethylenimine-modified BC, MgO_2-modified BC, Al(III)-modified BC, H_3PO_4-modified BC, Fe-impregnated BC have been stated to exhibit considerably higher adsorption and removal performance than pure BC toward heavy metal, especially for Cr(VI) and As(V). Biochar was soaked in $FeCl_3$ solution to make attached with it. After impregnation it was dried in oven and stored in zip lock bag for further use. Details are

mentioned in Chapter 3.

2.5.1 Washing of FeCl₃ solution

During formation of $FeCl_3$ solution, pallets of NaOH was added to lower pH Filtration was done using Whatman filter paper and fabric also as washing and then squeezing Fe using cloth can removes iron in better way. Washing was done using DI water up to 11-15 times to lower the pH of adsorbent to neutral. It was believed that hydrolysis of Fe salt would appear during the impregnation of Fe^{+3}

2.6   Application

2.6.1   Determination of Chromium using Colorimetric Method

Colorimetric method was used to find the concentration of Chromium. Following reagents were used in experimentation for application of modified biochar.

2.6.2   Reagents and Solutions

DI water:

Deionized water was used as reagent to prepare solution and it was purchased from chemical store.

Stock solution of Potassium dichromate:

Stock solution was prepared by dissolving 141.4 mg or 1.1414 g of dried $K_2Cr_2O_7$ (analytical grade) within reagent H_2O and then dilute to 1 L (1 mL = 50 µg Cr). The working solution was then made with stock solution by adding distilled water to obtain concentration of 20 mg/L using dilution formula.

Formulation of 1 M NaOH and 1 M HCl Solution

HCl solution were compose by disintegrating 4.13 mL of HCl in 100 mL deionized water and NaOH (sodium hydroxide) was compose by dissolving 400 mg of NaOH in 100 mL deionized water. Both solutions handed for the adjustment of pH.

Working solution of Potassium dichromate:

Dilute 10.00 mL $K_2Cr_2O_7$ of stock solution up to 100 mL in Erlenmeyer flask (1 mL = 5 µg Cr).

Sulfuric acid (H_2SO_4):

Dilute 10 mL of reagent grade of H_2SO_4, up to 100 mL using reagent water prepared above.

1,5-diphenylcarbazide solution:

Solution preparation was mentioned in start of methodology.

Acetone

Acetone of Reagent grade was used for the formation of diphenyl carbazide solution.

Procedure

First calibration curve was made, by adding 0.1, 0.2, 0.3- 2.2 mL of Cr (VI) and 0.25 mL (5 drops) of H_3PO_4 with pH of solution up to 2 or less than 4. Now transfer this solution in 100 mL volumetric flask and add 2 mL of DPC solution and set it for 4-5 minutes for complete dissolution. For taking absorbance value UV-spectrophotometer was used at wavelength of 540 nm. First reference sample was analyzed and sample solution (Alderson, J. Charles & Wall, 1992). Details and curve are mentioned in discussion section.

2.7   Kinetics Study

Kinetics study reveals that how adsorption had taken place over a period. For this reason, different models can be made to check and evaluate this phenomenon either it is chemical or physical adsorption. It can be checked by coefficient of determination (R^2) value which explains coherency between independent and dependent value. In this work Pseudo 1st and 2nd order kinetic models were made and proves that it has both Physisorption and Chemisorption phenomenon in it. Pseudo 1st indicate physisorption while pseudo 2nd order reveals chemical adsorption. Equation for pseudo 1st order kinetics

$$\log (q_e\text{-}q_t) = \log q_e - \frac{k_1\, t}{2.303}$$

Equation for pseudo 2nd order kinetics

$$\frac{t}{qt} = \frac{1}{k_2\, q_{2e}} + \frac{t}{qe}$$

Adsorbed chromium is represented by qt (at specific time), and qe (at equilibrium), k_1 and k_2 are constants for 1st and 2nd order kinetics.

2.8   Sample Preparation for Characterization

2.8.1   Sample Preparation for SEM-EDX

SEM provides images of high resolution by imparting electron bean and detect the secondary backscatter beam of electron. Advanced SEM machine have EDX device attached to them. For Scanning Electron Microscopy, sample must be conductive and dry. Sample preparation starts by pealing aluminum mounting peel carbon sticker and pressing the specimen onto exposed black carbon surface gently. Now specimen was added to the device hole. Electron microscopy just sees the surface of sample which sticks properly on to sticky area. So, it`s very important to place minute chunks of specimen. Then sample was secure to the mounting pin by turning side

mount screw gently and properly. At one time 3-5 samples can be placed in one run of machine. After this, fix specimen stub to the calibration slab, this sample placed in sputter coater to obtain a conductive surface. For coating gold and silver metals are used, with a layer thickness of 1-10 nm. Results of living samples can only be obtained. Now computer can show the images of under analysis sample, first image of surface can be taken at different micrometers then Energy Dispersive X-ray spectroscopy device provides composition and quantitative information of sample. In this way, sample is prepared for SEM and EDX results were taken.

2.8.2 Sample Preparation for FTIR

First clean the capsule press system (sample holder) with chloroform and dry them with tissues. For sample preparation KBr pallet formation method was used. KBr become transparent when high pressure is applied on to it, in the range of 4000-400 nm and it`s transmittance is 100%. Dry samples are used in FTIR analysis. For sample preparation first sample small amount of potassium bromide was placed in pallet dice to fill it`s full surface approximately of 2-3 layers, around 150 g. too much KBr used can make bad spectra data. Press the KBr plate by evacuable pallet press and hold 15 seconds to make perfect and smooth pallet. Now loose pallet dice and add very little amount of sample on to the KBr plate. Compress the sample and KBr pallet by bolt press and a pair of dice again together and hold for a minute. Keep the pressure at 10 metric tons for 1 minute after applying pressure. Take out and disassemble the pallet die. Lastly transfer the KBr pallet holder for analysis.

2.8.3 Sample Preparation for Brunauer, Emmett and Teller (BET)

Sample preparation begin by doing weight of sample, recommended weight is 0.1-0.5 and then degassing, it means to put sample in a tube and remove moisture and gas particles for the sample chamber tube. For ideal analysis 24 hours are required for degassing and then analysis of sample start. Degassing time and temperature vary with composition and state of specimen. For sugarcane bagasse and peanut shells powders both modified and non-modified degassing time was 24 hours and temperature were 90°C. Followed by degassing, sample is then placed in analyzing chamber for surface area analysis. BET machine automatically analyze single pot surface area, total surface area and generates results.

CHAPTER 3
RESULTS AND DISCUSSION

3.1 General Information

This section covers all Experimental work analysis, discussion, and it`s results. Selection of this method was based upon economic factor and generation of waste at the end of process. By following this way of heavy metal removal in lesser time and effort high efficiency can be obtained.

3.2 Discussion

3.3 Recovery of Adsorbent

Recovery of adsorbent is possible during whole experimentation, in such a way that after filtration if the adsorbent dried it can be again used and gives efficiency much higher as well.

3.4 Biochar Modification

Ferric chloride modification method was used as it is chosen after literature study. As Chromium is negatively charged specie and $FeCl_3$ is positively charged salt, it gives biochar extra positive charges which helps in efficient removal of metal (Jiang et al., 2022). Among modification methods, saturation of BC using Fe believed to be one of the promising methods to enhance adsorption of metals. Activation / Modification was done using $FeCl_3$ which react with oxygen and make iron oxide which is well accepted method for the modification of adsorbent (biochar). Iron oxide has hydroxylated surface which have high functional group of -OH and provide high adsorption capacity for metal removal like Cr^{+6}. For modifications iron having oxidation state of II and III are well used, Fe^{+3} is preferable. $FeCl_3$ has powerful buffering capacity. It provides H^+ ions in solution and make colloids of ferric hydroxide. Fe^{+3} oxide/hydroxide colloid has high chromium removal efficiency at neutral pH (Yi et al., 2021). Iron chloride is a conventional chemical reagent, that has robust buffering capacity. For activation 10 g of biochar (PSP and SBP) was mixed with 500 mL $FeCl_3$ solution with constant stirring at 70°C for 2 h at pH 11, so that biochar and make bond with $FeCl_3$ at basic pH as reported by (Solangi et al., 2020) (figure 2.5). This solution was then washed and filtered using cloth to remove iron from solution and to maintain pH at neutral. Filtered solution was now placed in crucible and kept in over at 90°C for drying for 24 hours.

3.5   Standard Calibration (SC) curve

Standard calibration curve was made using working solution originally made from Cr (VI) stock solution. By adding 0.1 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, 1 mL, 1.2 mL, 1.4 mL, 1.6 mL, 1.8 mL, 2 mL, 2.2 mL of Cr(VI) working solution taken with the help of micro pipet and placed in 250 mL Erlenmeyer flask and fill the flask to 100 mL DI water, five drops of H_3PO_4 and 2 mL of DPC. Absorbance values were taken with correspondence to Cr (VI) concentration are mentioned in table 3.1

Table 3.1   Absorbance values for Standard Curve

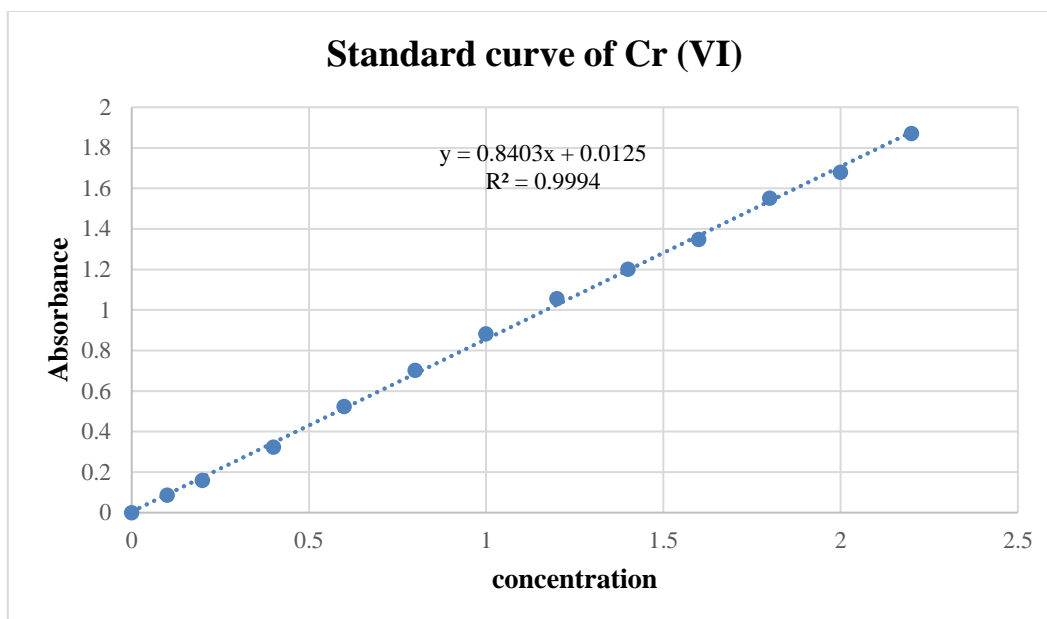| Absorbance values for Standard Calibration Curve	
Concentration (mg/100mL)	Absorbance
0	0
0.1	0.0865
0.2	0.1583
0.4	0.3234
0.6	0.5241
0.8	0.7026
1	0.8812
1.2	1.0551
1.4	1.2016
1.6	1.3485
1.8	1.552
2	1.6799
2.2	1.8706

Figure 3.1   Cr (VI) Standard Calibration Curve

3.6   Adsorption Graphs

Batch experimentation for Cr (VI) removal was done by taking 10 mL of Cr (VI) from stock solution in 250 mL Erlenmeyer flask with 0.3 g of Activated Carbon and fill distilled water up to 100 mL. Flask was entirely hermetically sealed and stirred at speed of 150 rpm in a temperature 24 °C controlled by Shaker as it is ideal temperature for removal as reported by (Yi et al., 2021), Thermolyne M49120 - 126 for 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180 min. Experimentation was done by keeping, adsorbent dosage 0.3 g, pH 2, Cr (VI) concentration 20 mg/L constant and time factor as variable. At pH 2 Chromium exists in the form of chromium hydroxide (HCrO⁻), which has more adsorption capacity as compared to other forms of chromium. Time was taken as fixed parameter as in the whole experiment time and pH were main variable. Residual concentration of Cr (VI) in the self-made contaminated aqueous solution was filter by vacuum filtration assembly and analyzed using UV-Visible spectrophotometer (Specord 200 plus Analytikjena Germany) with adsorption at 540 nm. Absorption capacity (qt (mg/g)) and the removal percentage was calculated using following equation:

$$q_t = \frac{(Co - Cf)V}{m}$$

$$\% \text{ removal} = \left(\frac{Co - Cf}{Co}\right) 100$$

$$\% \text{ removal} = \left(\frac{initial\ conc - final\ conc}{initial\ concentration}\right) 100$$

Here "C_o" and "C_f" indicate the initial and residual metal concentrations (mg L^{-1}) respectively, "v" is solution volume (mL), and "m" is mass of adsorbent (g) used. Values for Percentage removal and graph is presented in table 3.2, figure 3.3 .

Table 3.2 Cr (VI) Removal using Modified SBP

| Removal of Cr(VI) using Modified Sugarcane Bagasse					
Cr (VI) Initial conc (mg/L)	Cr (VI) Finial conc (mg/L)	time (min)	Adsorption Capacity (qt)	Absorbance (mol/L)	Cr (VI) Removal (%)
0	0	0	0	0	0
20	2.53	10	0.13	0.2134	87.33
20	2.43	20	0.19	0.2045	87.87
20	1.45	30	0.22	0.1232	92.73
20	1.32	40	0.32	0.1119	93.41
20	1.11	50	0.38	0.0936	94.5
20	0.87	60	0.41	0.0748	95.63
20	0.83	70	0.53	0.0709	95.86
20	0.83	80	0.65	0.0708	95.87
20	0.69	90	0.67	0.0593	96.56
20	0.6	100	0.69	0.0523	96.98
20	0.6	110	0.71	0.052	97.01
20	0.52	120	0.74	0.0453	97.4
20	0.51	130	0.77	0.0442	97.46
20	0.4	140	0.78	0.0356	97.98
20	0.44	150	0.93	0.0382	97.82
20	0.32	160	1.08	0.0285	98.4
20	0.25	170	1.19	0.0227	98.75
20	0.21	180	2.23	0.0192	98.96
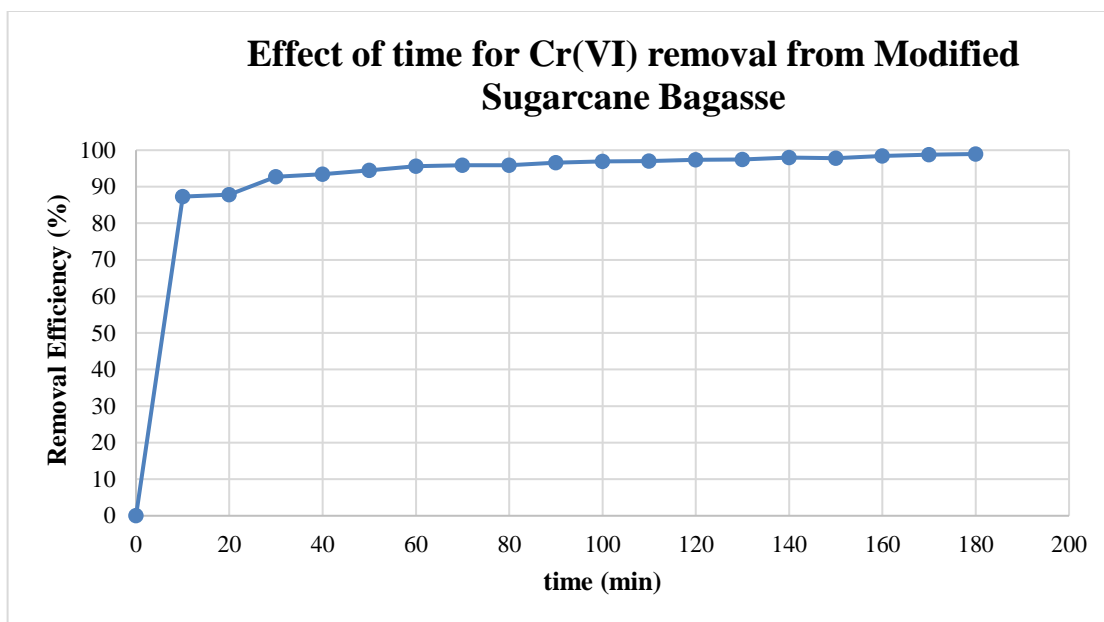
Figure 3.2 Effect of time for Cr(VI) removal using Modified SBP (Adsorption conditions: temperature = 28°C, Cr(VI) concentration = 20 mg/L, absorbent dosage = 0.3 g, pH = 2)

Same sample treatment was applied with Activated Peanut Shell Powder (PSP) with absorbent dose of 0.3 g at pH 2, Cr (VI) concentration of 20 mg/L and variable time of 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180 minutes. Following is removal percentage graph of APSP table 3.3

Table 3.3 Removal using Modified PSP

Removal of Cr(VI) using Modified Peanut shell Powder					
Cr (VI) Initial conc (mg/L)	Cr (VI) Finial conc (mg/L)	time (min)	Absorption Capacity (qt)	Absorbance (mol L^{-1})	Cr (VI) Removal (%)
0	0	0	0	0	0
20	1.97	10	0.28	0.1894	90.23
20	1.68	20	0.31	0.1768	90.64
20	1.54	30	0.43	0.1724	91.17
20	1.37	40	0.51	0.1599	91.51
20	1.24	50	0.62	0.15233	92.56
20	0.22	60	0.63	0.13731	92.92
20	0.19	70	0.71	0.11284	94.02

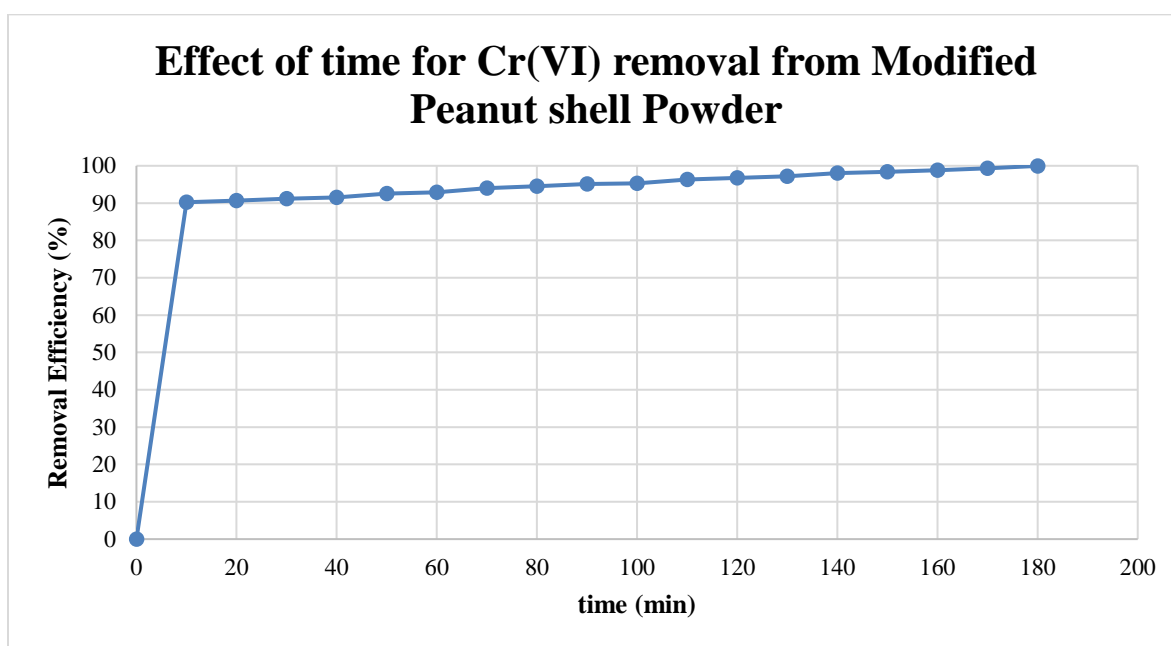| 20	1.08	80	0.73	0.10386	94.56
20	0.97	90	0.79	0.09461	95.11
20	0.93	100	0.83	0.09132	95.31
20	0.73	110	0.88	0.07411	96.33
20	0.65	120	1.01	0.06742	97.4
20	0.56	130	1.09	0.06539	97.46
20	0.38	140	1.30	0.04451	98.23
20	0.37	150	1.33	0.0398	98.38
20	0.22	160	1.48	0.0318	99.07
20	0.13	170	1.56	0.024	99.31
20	0.05	180	1.67	0.013	99.97

Figure 3.3 Effect of time for Cr(VI) removal using Modified PSP (Adsorption conditions: temperature = 28°C, Cr(VI) concentration = 20 mg/L, absorbent dosage = 0.3 g, pH = 2)

Before any modification and experimentation Thermal Analysis of biomasses was done to check the highest temperature for degradation of biomasses. Then after $FeCl_3$ modification sample was analyzed by SEM-EDX, FTIR, and Brunauer, Emmett and Teller surface area analysis techniques. At the end for confirmation of results adsorption kinetics models were implemented and results are discussed below.

3.7 Figures & Graphs

3.7.1 Thermogravimetric Analysis (TGA)

TGA explained thermal degradation performance of PSP and SBP by thermal analyzer (TGA-50/50H SHIMADZU machine) was used for this analysis. Sample was examined at heating rate (10°C/min) from room temperature up to 550 °C in high purity N_2 gas with the flow rate of 200 mL/min was used for creation of inert atmosphere in system. Replicate analysis was performed thrice and then mean values have been reported, with approximate error of ± 0.5 in absolute value. At temperature less than 100°C moisture content loss from both samples. Existence of the three sectors of mass loss in TGA, first one is around 100˚C which indicates water loss, and remaining two regions represents one around 200˚C - 350˚C and other 350˚C - 500˚C owing to the degradation of organic matter as reported by (Machado et al., 2018). Thermogravimetric Analysis of sugarcane bagasse (Saccharum officinarum) powder starts to degrade at 283°C, and Peanut shell powder (Arachis hypogea) of about 376°C shown in Figure 3.5. Complete decomposition occurs at 544°C of PSP and on 569°C for SBP. It is stated that degrading temperatures of hemicellulose 315 - 400°C, lignin 160 - 900°C, cellulose 200 - 315°C (Heating et al., 2015). It is noted that first peak appears at 319°C is because of hemicellulose thermal decomposition of raw SB and other peak appear on 367°C is due to degradation of cellulose. At higher temperature lignin of sugarcane bagasse deteriorate. TGA curve, presented in figure 3.5 shows that 78 wt% of SB thermally degrade when temperature of reaction is 410°C. It indicates that pyrolysis of SB should be performed at temperature above 410°C. For this purpose, pyrolysis of SB in this research was done at 500°C.
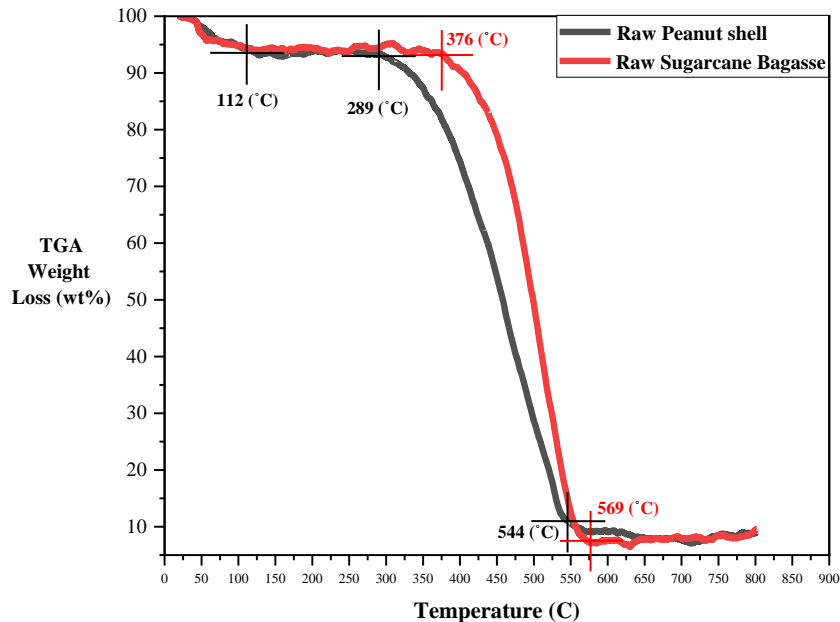
Figure 3.5 TGA thermogram of Raw SBP & PSP

Peanut shell powder (Arachis hypogea) exhibit more mass loss, it starts to degrade at 200℃ and complete mass loss occurs at 530℃. Maximum weight loss was done during the temperature range of 300 - 500℃.

3.7.2   Scanning Electron Microscope (SEM)

Morphological study, visual display can be studied by SEM analysis model, JEOL- JSM-6490A Analytical Scanning Electron Microscope, SCME, NUST which shows surface figure of biomasses Figure 3.6, 3.7. Following are SEM images of naturally occurring biomasses PSP and SBP. It is clearly seen that both biomasses have rough surface. Raw and unmodified sugarcane bagasse and peanut shell surface is full of cracks and grooves.
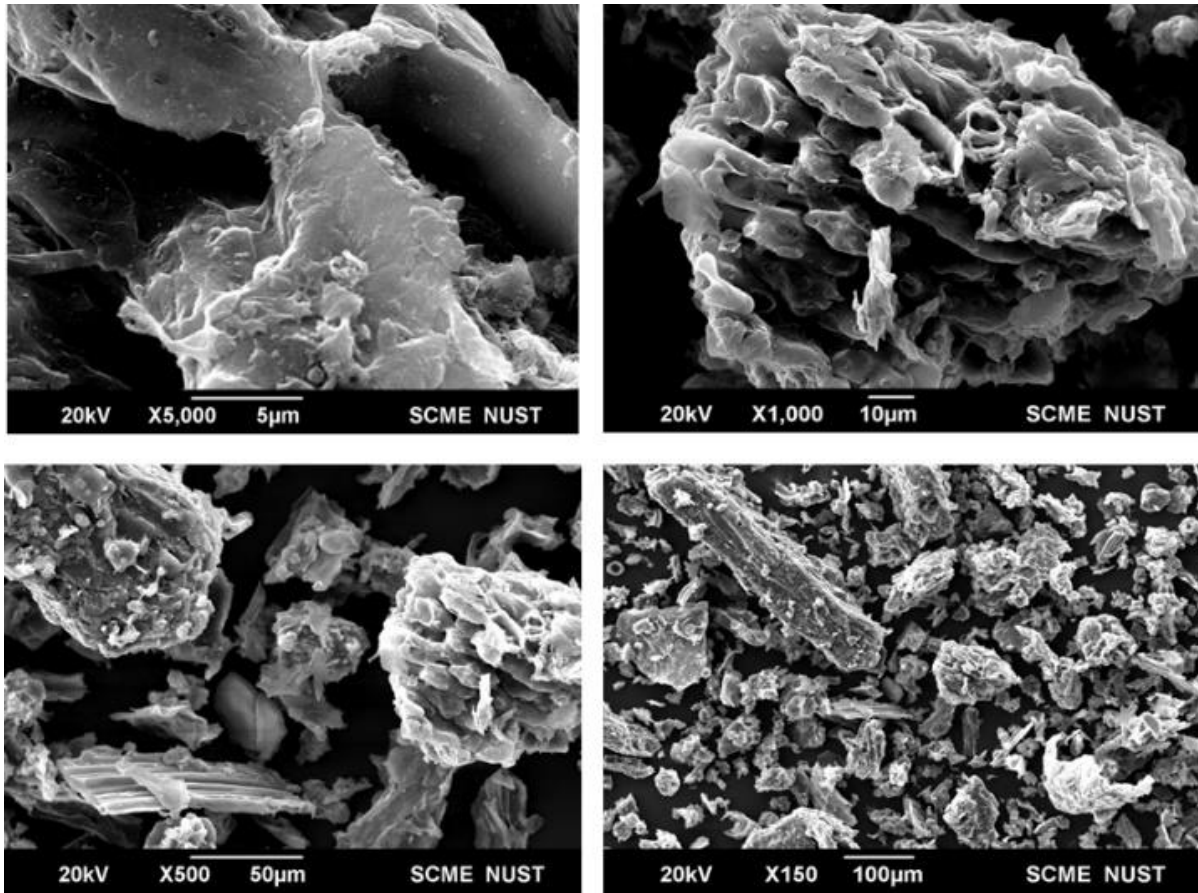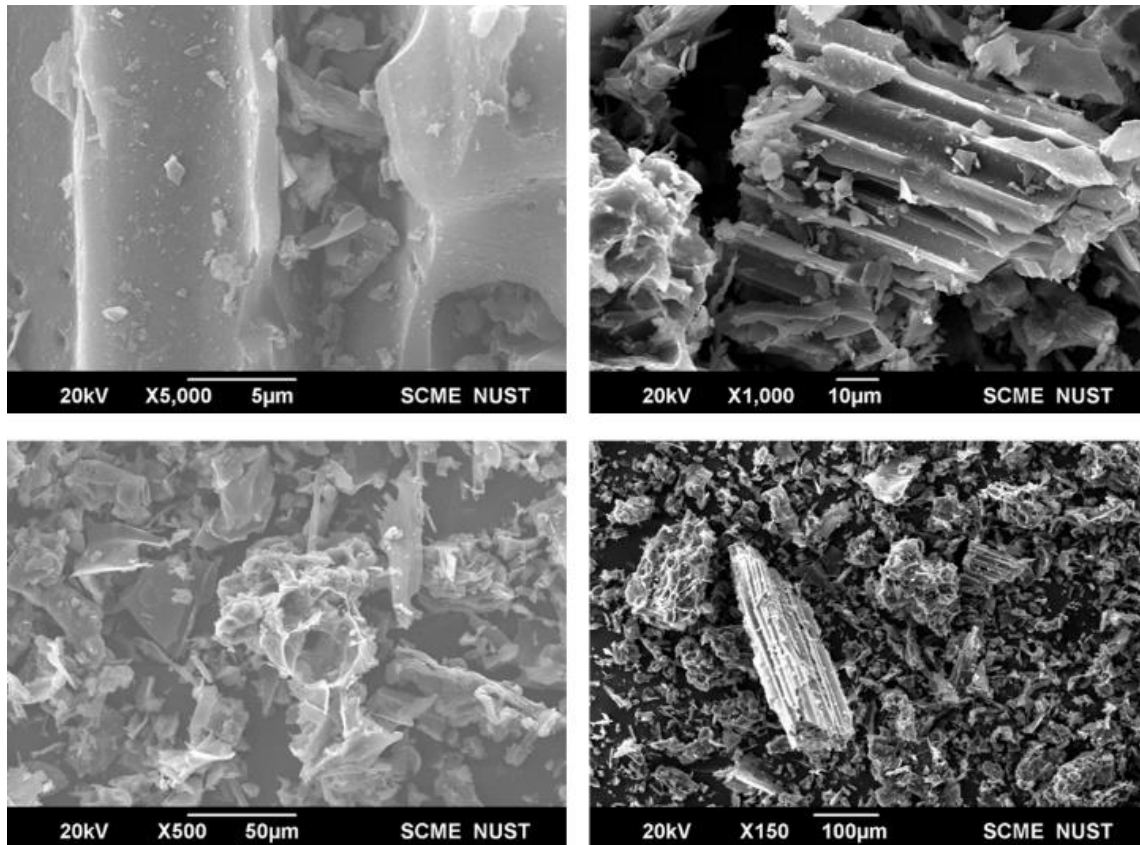
Figure 3.6 SEM image of Raw PSP

Figure 3.7 SEM of Raw SBP

Following are images of FeCl₃ Modified PSP and SBP, Figure 3.8, 3.9 and proves that surface after modification becomes smooth. It was observed that Fe has fully embedded into biochar which increases the exchange capacities of ions, (Min et al., 2020). Images are shown taken on different resolutions and magnifications. It can be seen that after FeCl₃ modification, surface roughness decreases, pore size decreases and smoothness increases. It indicates successful loading of Fe^{+3} particles on biochar.
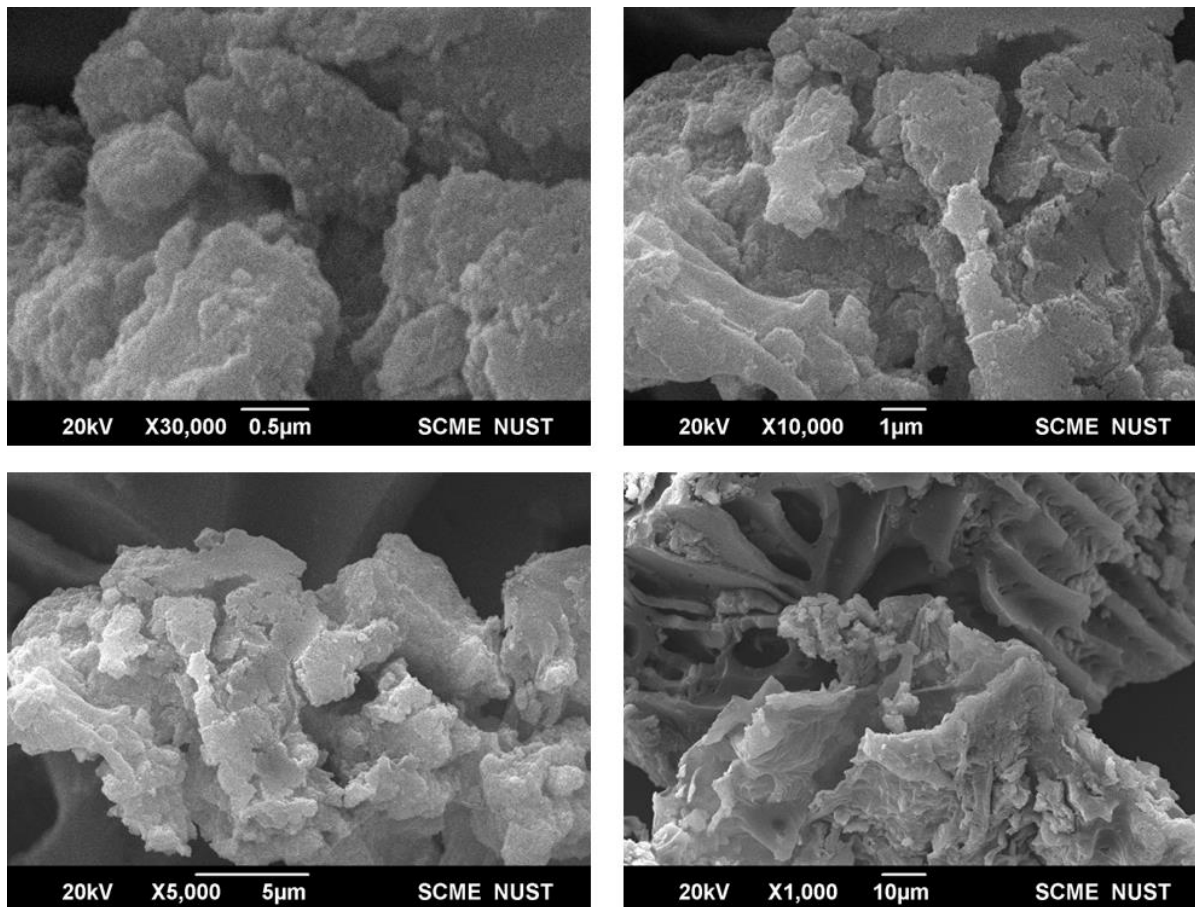
Figure 3.8 SEM image of FeCl$_3$ Modified PSP
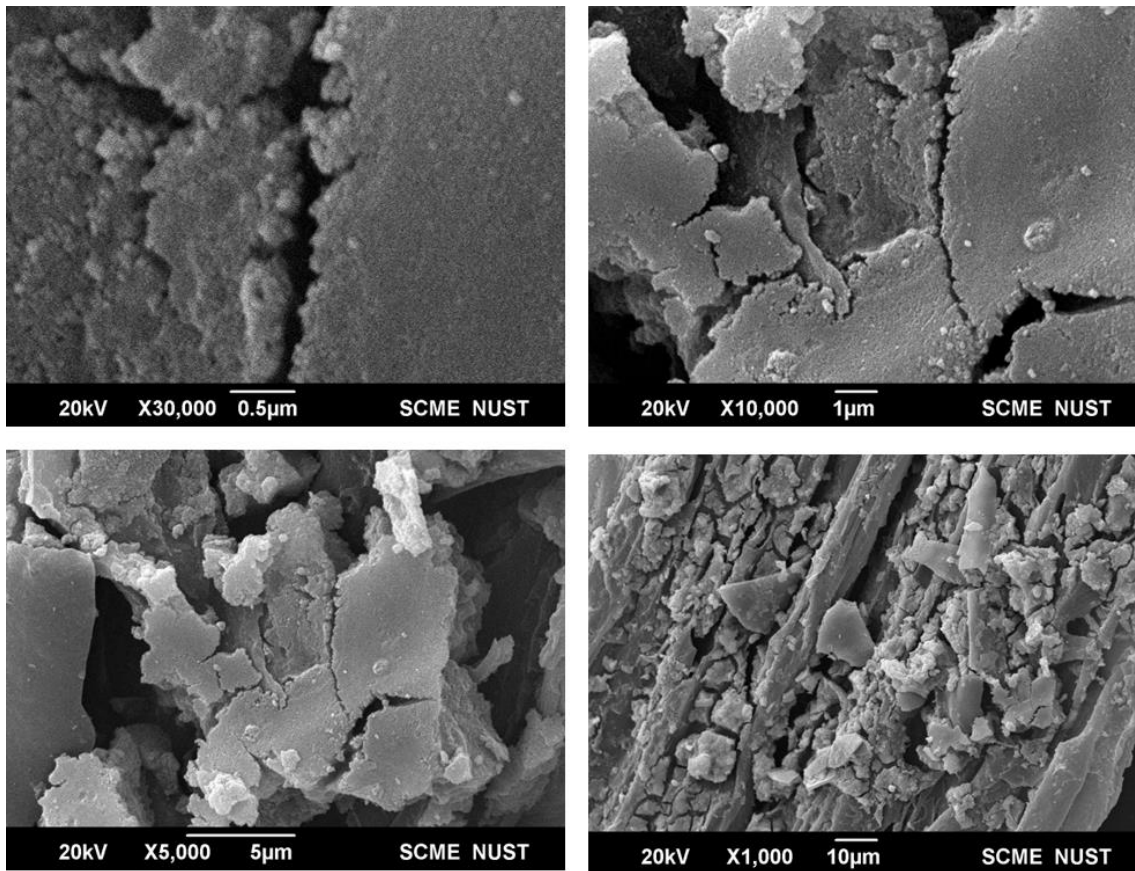
Figure 3.9 SEM image of FeCl$_3$ modified SBP

3.7.3 Energy Dispersive X-ray spectroscopy (EDX)

EDX spectra (Z2-i7 Analyzer SCME, NUST) of PSP and SBP are following, as they are natural biomasses So, results are displayed as it was taken. EDX reveals elemental composition. Following are EDX of four sample: 1. PSP 2. SBP 3. FeCl$_3$ Modified PSP 4. FeCl$_3$ Modified SBP. Modified biochar was having peak of Fe in them which confirms modification and impregnation of iron into biochar. Largest peak is of Carbon, at 2.5 Au (gold) peak appears. Au was used for coating on samples during elemental analysis. It can be seen from figure 3.10 and 3.11 that biomass contains 70-80% carbon content and 13-15% oxygen and other elements are in very minute concentration.
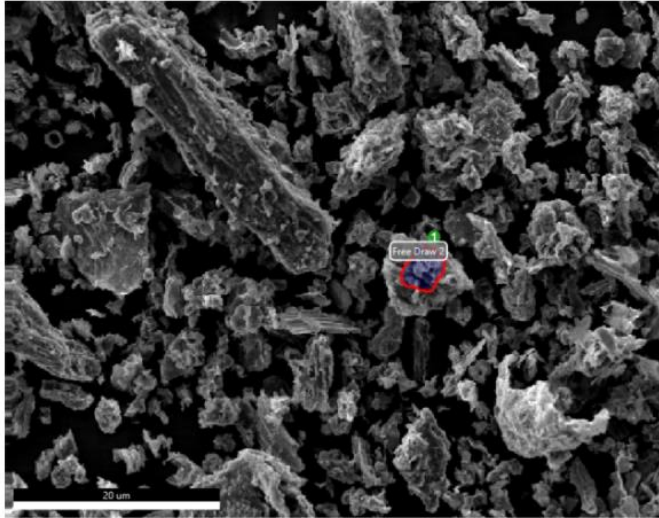
eZAF Quant Result - Analysis Uncertainty: 16.77 %

Element	Weight %	MDL	Atomic %	Error %
C K	70.8	3.02	82.2	11.1
O K	14.8	0.66	12.9	14.1
Al K	0.6	0.14	0.3	16.0
Si K	1.7	0.13	0.8	8.4
P K	1.1	0.17	0.5	6.8
S K	0.0	0.00	0.0	100.0
Cl K	2.5	0.17	1.0	6.8
K K	2.7	0.19	1.0	6.8
Ca K	1.0	0.22	0.3	16.4
Fe K	1.0	0.31	0.2	18.1
Cu K	1.7	0.44	0.4	14.1
Mo L	2.2	0.32	0.3	15.4
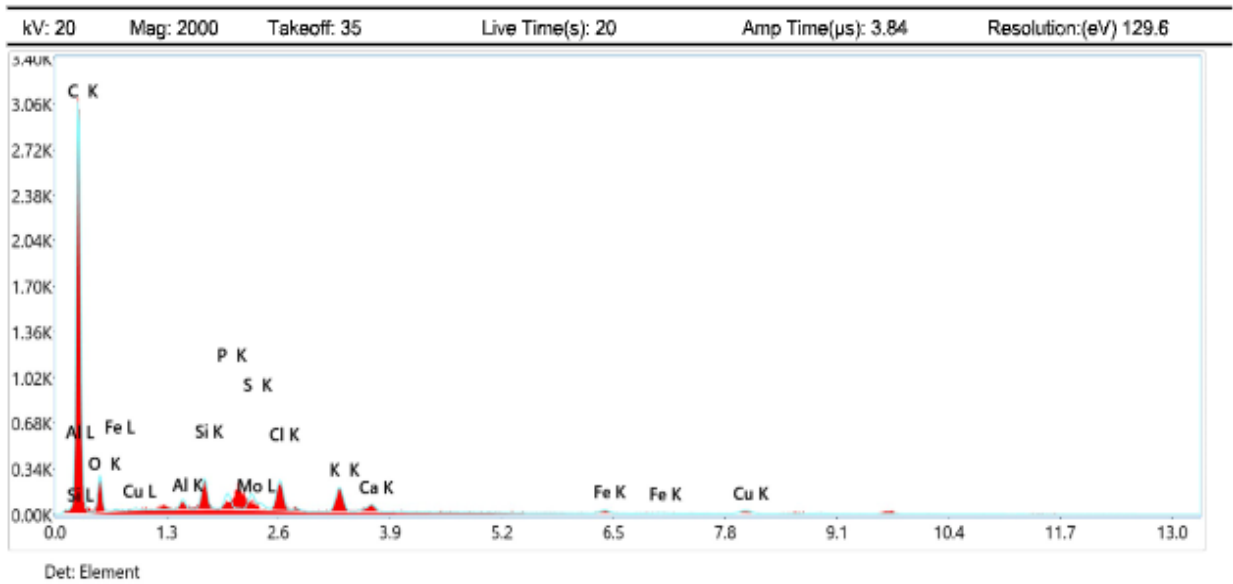
Figure 3.10 Energy Dispersive X-Ray Analysis of PSP
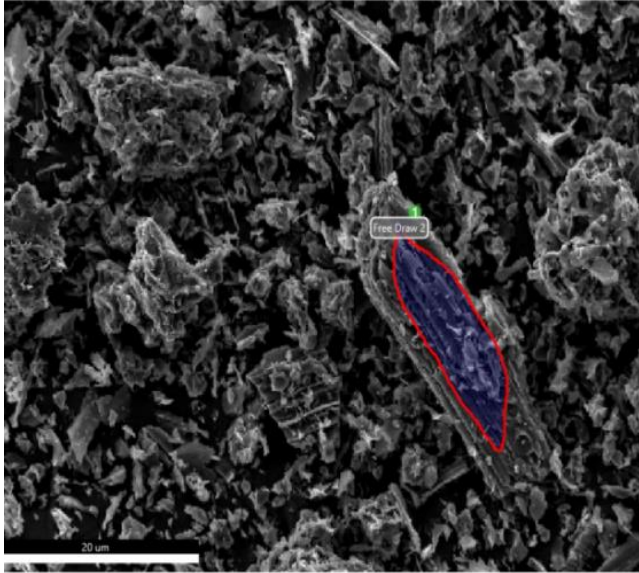
eZAF Quant Result - Analysis Uncertainty: 17.61 %

Element	Weight %	MDL	Atomic %	Error %
C K	75.9	2.73	84.7	10.8
O K	13.5	0.53	11.3	14.4
Na K	1.3	0.23	0.8	15.1
Si K	1.2	0.13	0.6	10.4
P K	1.4	0.16	0.6	6.0
S K	1.1	0.16	0.5	12.5
Cl K	0.9	0.19	0.4	15.2
K K	1.2	0.19	0.4	13.6
Ca K	0.7	0.22	0.2	19.2
Cu K	2.7	0.59	0.6	12.9
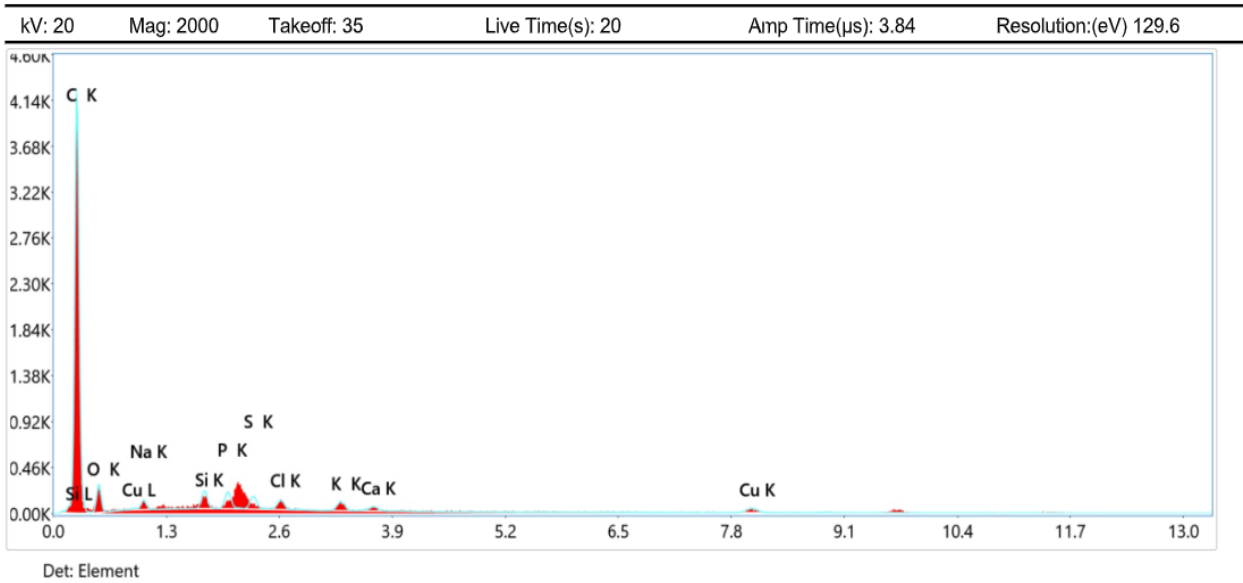
Figure 3.11 Energy Dispersive X-Ray Analysis of SBP

EDX of $FeCl_3$ modified biomasses shows the presence of iron attached with it. Figure 3.12 and 3.13 shows all the elements present in adsorbent after modification.

34
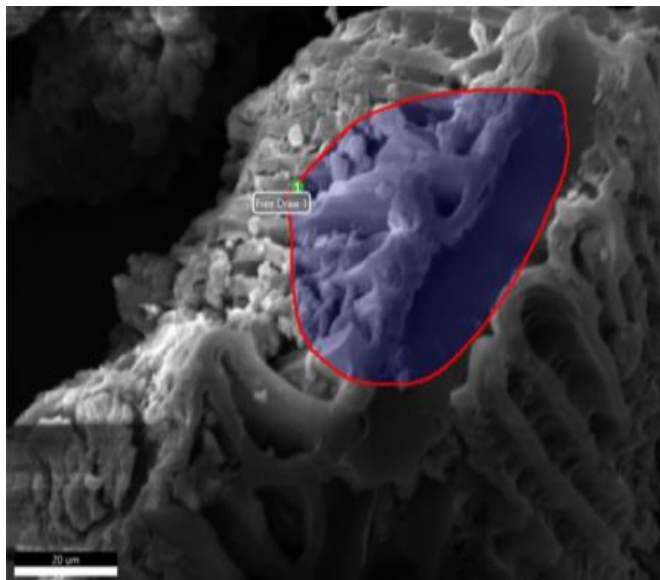
eZAF Quant Result - Analysis Uncertainty: 17.71 %

Element	Weight %	MDL	Atomic %	Error %
C K	55.2	0.17	75.6	10.1
O K	20.6	0.34	21.1	11.4
Ca K	0.3	0.11	0.1	20.6
Fe K	5.4	0.20	1.6	4.3
Au L	18.5	1.03	1.5	10.5

Figure 3.12 EDX image of FeCl$_3$ modified PSP

eZAF Quant Result - Analysis Uncertainty: 12.95 %

Element	Weight %	MDL	Atomic %	Error %
C K	37.5	1.06	65.2	10.8
O K	19.8	0.33	25.8	11.1
K K	0.5	0.12	0.2	14.9
Fe K	14.3	0.21	5.3	3.5
Co K	0.4	0.23	0.2	22.0
Zn K	1.2	0.32	0.4	22.6
Au L	26.4	1.35	2.8	10.3
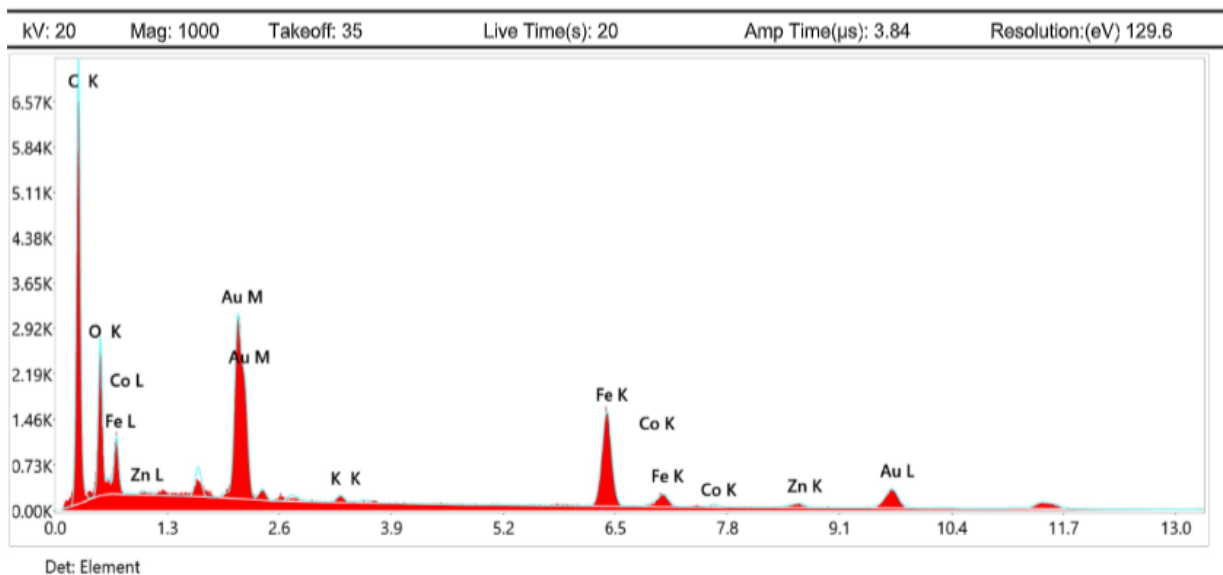
Figure 3.13 EDX image of $FeCl_3$ modified SBP

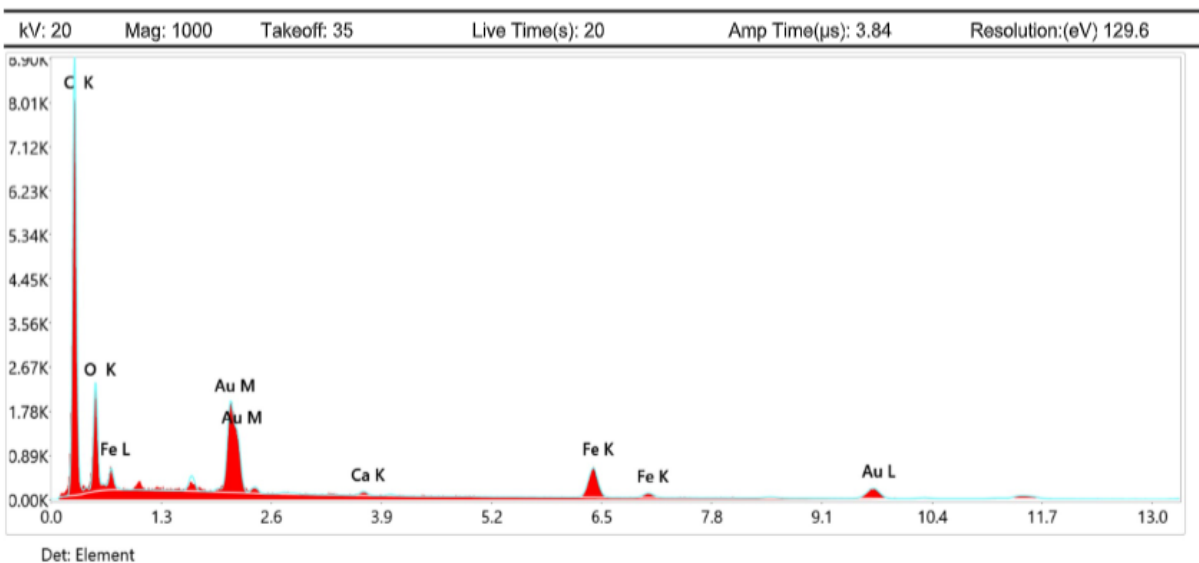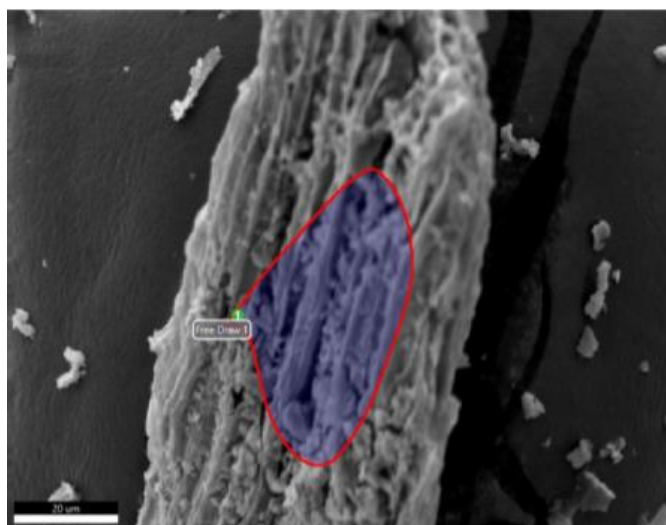### 3.7.4   BET (Brunauer, Emmett and Teller) Analysis

The BET (Brunauer, Emmett and Teller) analysis generally used to estimate the gas adsorption data and generate specific surface area value result which is expressed in units (m^2/g). This analysis was done using Quanta chrome Nova Win Instrument version 11.05 from USPCASE, NUST. The result of BET analysis shows that value of raw and $FeCl_3$ modified peanut shell powder are 39.830 m²/g and 10.1157 m²/g respectively and raw sugarcane bagasse and $FeCl_3$ modified have 25.268 m²/g and 18.7709 m²/g respectively, presented in Table 3.4. Lesser the particle size of carbon, greater is the rate of diffusion and adsorption (Xu et al., 2011). The decrease in surface area value for modified biomasses was due to using Ferric chloride which

36

block pores of biochar (Yi et al., 2021). As biochar is negatively charged, and iron has positively charged that is why the removal efficiency was 99.97% using $FeCl_3$ activation method.

Table 3.4 Surface area Analysis

Sample	Single point SA	BET-SA	Pore Volume	Pore Radius
Raw Peanut shell Powder	53.2132 m²/g	39.830 m²/g	0.054 cm³/g	16.044 Å
FeCl$_3$ PSP	10.0048 m²/g	10.1157 m²/g	0.005144 cm³/g	21.101 Å
Raw Sugarcane Bagasse	49.6679 m²/g	25.268 m²/g	0.036 cm³/g	16.155 Å
FeCl$_3$ SB	18.5476 m²/g	18.7709 m²/g	0.0134 cm³/g	29.7992 Å

SA: Surface Area, PSP = Peanut shell Powder

3.7.5 FTIR ANALYSIS

Fourier Transform InfraRed (FTIR) technique applied to examine chemical structure and to validate the functional groups from adsorbent surface. For acquiring absorption spectra, all samples were furthermore grounded to roughly 0.5 wt% with spectroscopic grade of KBr powder for homogenization and pallet formation. Results of analysis are presented in Figure 3.10 and 3.11. Discs (12.7 mm I.D and about 1 mm in thickness) were prepared using manual hydraulic press at 1000psi (parts square per inch) for a pressing time of 0.5 min. The acquired result is shown in Fig and analysis was done using Perkin Eimer Spectrum 100 FT-IR Spectrometer SCME, NUST with 400-4000 cm^{-1} with a resolution of 2 cm^{-1}. Here a broad peak appears at 3000-3700 cm^{-1} which unveils -OH group of ketone or aldehyde (Min et al., 2020b). The peak 2850-2930 represents -CH_2 aliphatic hydrocarbons vibrations and C-H group (Jin et al., 2018). Sharp intense peak observed at 1602 cm^{-1} is due to lignin aromatic rings of C=O and C=C. Intense peak in the region 1030-1364 was due to stretching C-O of lignin, hemicellulose and cellulose (Harripersadth et al., 2020). Peak at 555 and 472 were due to Fe modification and impregnation (Yi et al., 2021).
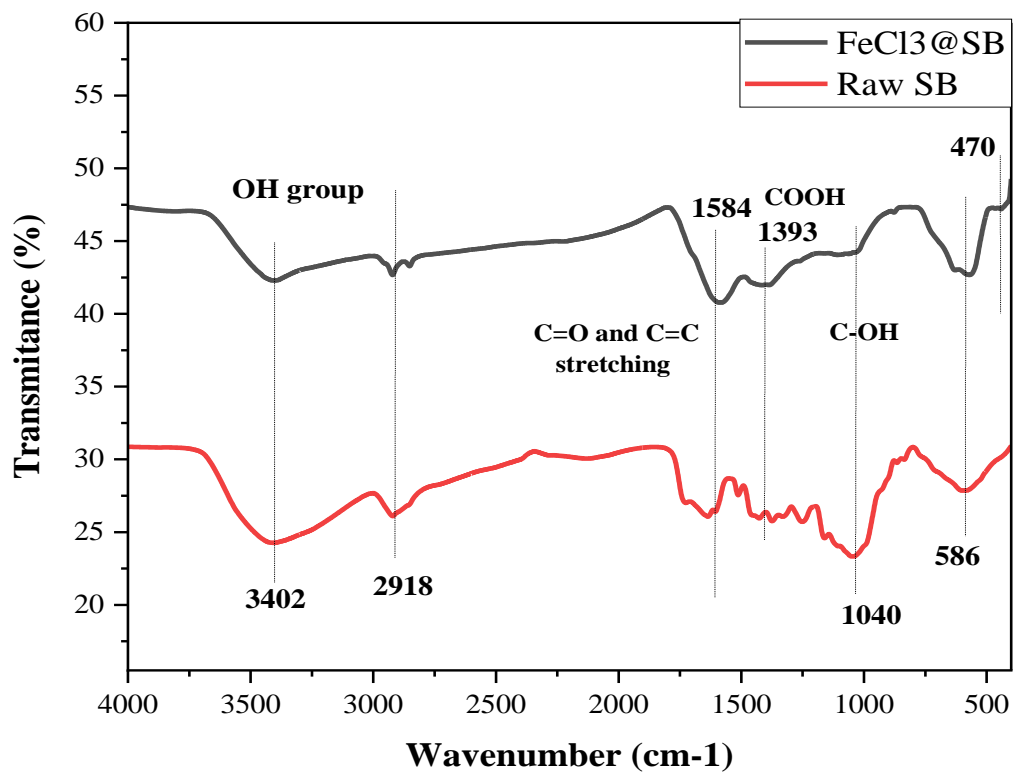
Figure 3.10 FTIR graph of Raw and Modified SBP
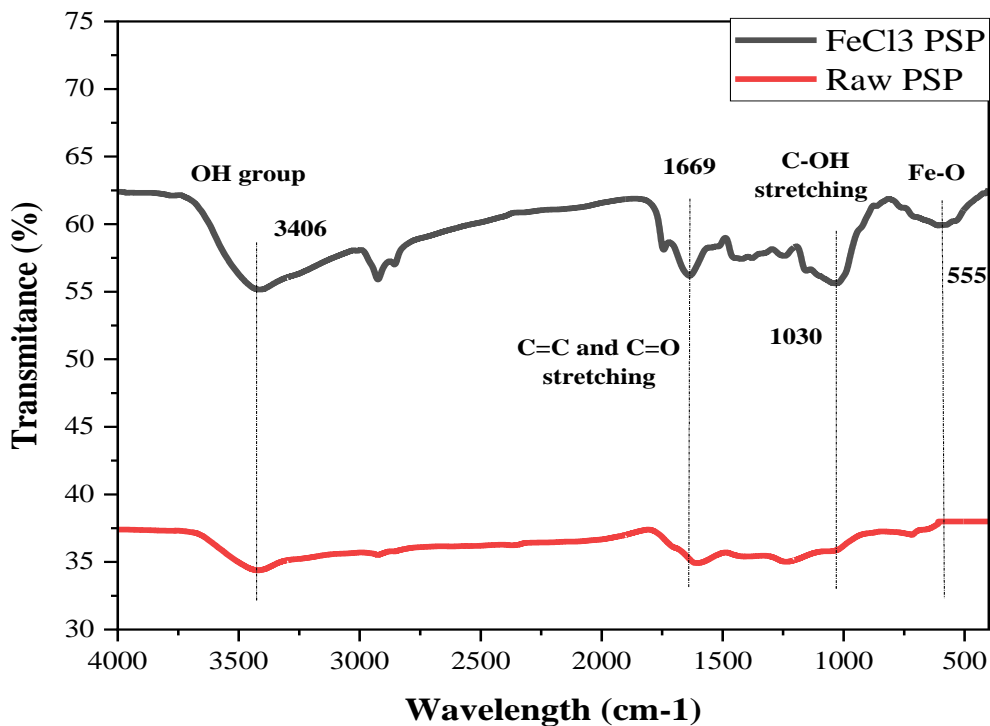
Figure 3.11 FTIR graph of Raw and Modified PSP

3.8 Adsorption Kinetics

To explain kinetics adsorption of Chormium models of Pseudo 1st order and 2nd order were used, models were drawn in Origin software using following equations:

$$Q_t = Q_e (1 + e^{-k1t})$$

$$Q_t = k_2 Q^2_e t / 1 + k_2 Q_e t$$

here Qt (mg/g) is deposited metal at time t (min), Qe (mg/g) is adsorbed metal at equilibrium. dynamics constants are k_1 (min^{-1}), k_2 (g/mg·min). For both models, value of R^2 and Chi-Square indicate error parameters. Equilibrium stage attain after 60 mints and best removal was at 160 mints.
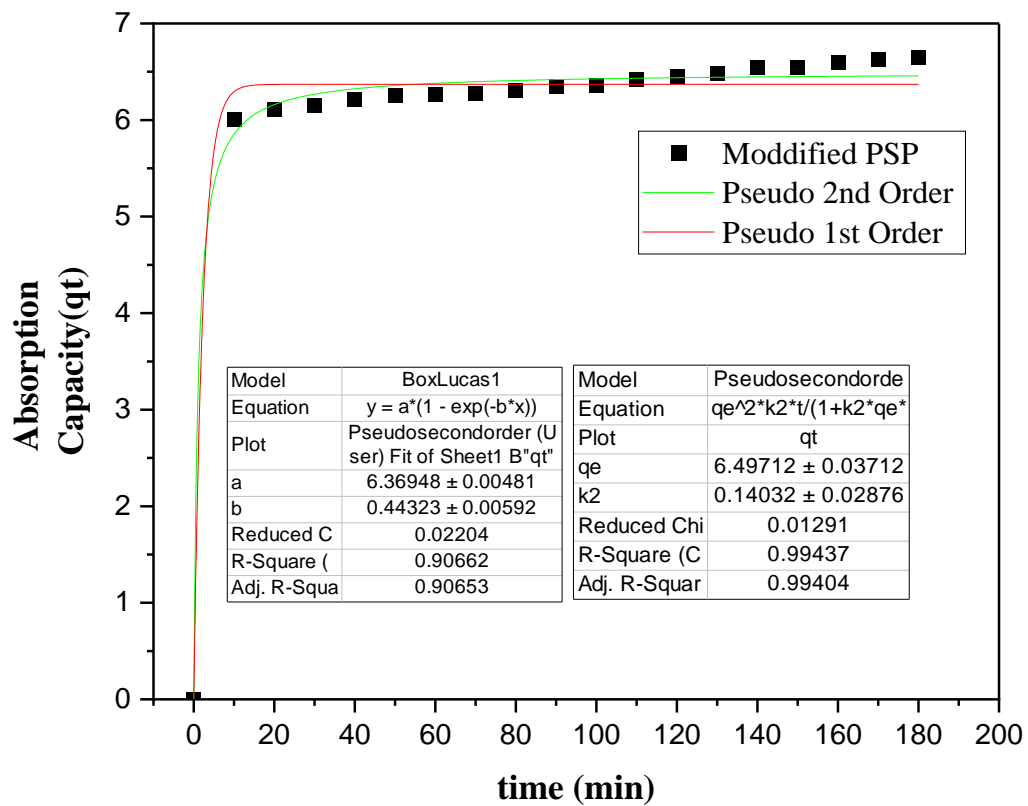
Figure 3.12 Pseudo 1st and 2nd order kinetics for Modified PSP
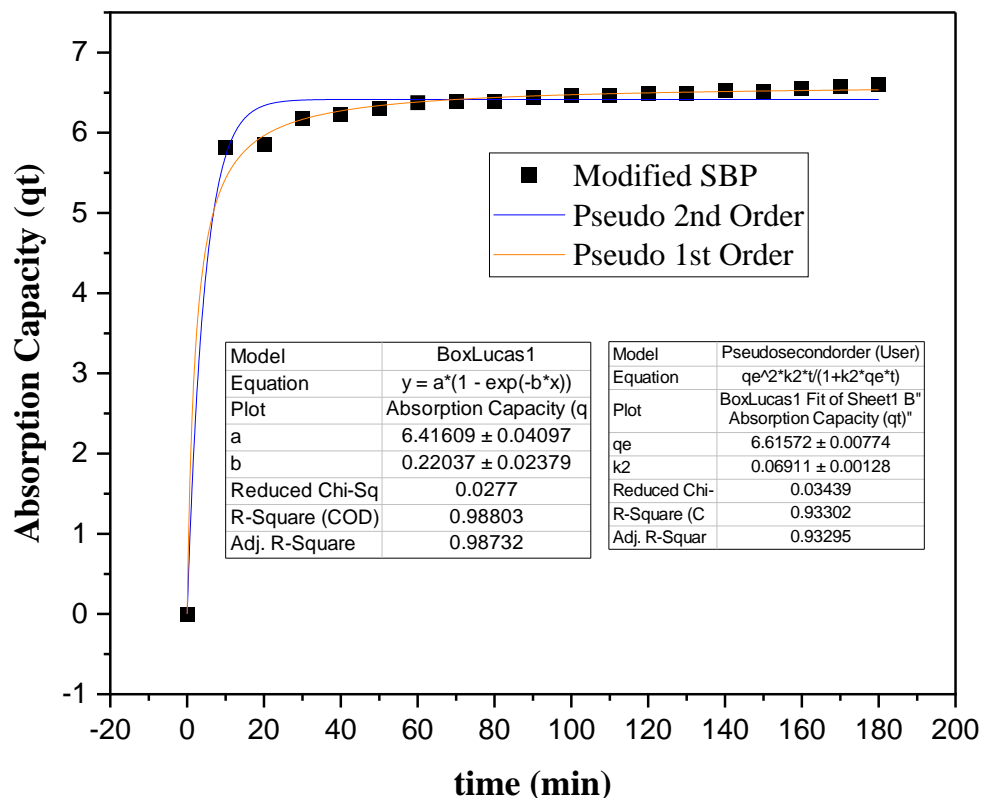
Figure 3.13 Pseudo 1st and 2nd order kinetics for Modified SBP

CONCLUSION

This was cheap technological solution for removal of Chromium heavy metal from water. $FeCl_3$ modified biochar was made using peanut shells and sugarcane bagasse. Comparative experimental study successfully reveals that carcinogenic heavy metal can be removed using $FeCl_3$ modified green waste biomasses up-to 98% as compared to modified sugarcane bagasse. To prevent Cr(VI) water pollution this adsorption-based phenomenon is of great importance and uses waste as raw material. For this purpose, two different biomasses i.e., PSP and SBP were collected which are abundantly available in all over Pakistan and used for Cr(VI) adsorption from synthetic polluted water. Removal percentage increases with time and was maximum at 180 mints with Cr (VI) concentration of 20 mg/L, pH 2 having adsorbent dose of 0.3 g and shaking speed 150 rpm. Hence, conclude that Peanut shells can be used for obtaining 99.99% Cr removal if modified by $FeCl_3$.

RECOMMENDATIONS

- There is need to adopt the easy and economical way, described as above for removal of carcinogenic heavy metal like Cr (VI) from at least drinking water. So, that people of developing and underdeveloped countries can also acquire their necessity.

- More work can be done in regard for heavy metals removal, for instance this lab scale experimentation if applied on larger scale it can be useful in high efficiency.

- Industrial effluents must be treated up to permissible limit before spilling into water or soil as well.

- This study can be further use by altering parameters like temperature, adsorbent dosage, pH, activating chemical, different green waste etc., and other parameters.

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