

PRODUCTION OF ACTIVATED CARBON FROM SEWAGE SLUDGE FOR THE  
REMOVAL OF LEAD FROM WATER

by

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## **Dedication**

Dedicated to beloved parents, sincere brother and sister, extremely supportive  
mentors!

## Abstract

Different activated carbons were produced from sewage sludge taken from Sharjah waste water treatment plant. Carbonization and activation were carried out in steam environment without an external flowing inert stream or in nitrogen environment. Sewage sludge was dried under sun before carbonization and solid KOH was added in between carbonization and activation steps. Maximum temperature reached for carbonization and activation was 700°C. In post treatment activated carbons were either washed directly with acid solutions (5M HCl or 5M HNO<sub>3</sub>), or were rinsed in soxhlet. Activated carbons were analyzed by sorption of nitrogen, Boehm titrations, pH measurement, thermal analysis (DTA and DTG analysis), ash content, scanning electron microscope and energy-dispersive X-ray spectroscopy mapping and adsorption of lead isotherms. In production of activated carbons from sewage sludge a total mass loss of 81 to 83 percent was observed. Nitrogen adsorption / desorption curves showed that most of the surface area was possessed by micro and meso pores with an average pore size of 25 Å. Carbonized samples possessed surface area less than 4 m<sup>2</sup>/g. Sewage sludge based activated carbons produced under nitrogen environment and steam environment exhibited surface area 1019 and 838m<sup>2</sup>/g respectively. pH experiments showed that carbonized samples were basic, activated carbons post treated with acid were acidic and activated carbon rinsed in soxhlet is basic. Boehm titration results were consistent with pH results and revealed the presence of high amount of surface functional groups in all sludge based carbons, 4 to 6 mmol/g. Carbonized samples possessed high ash contents up to 50 percent. Activation processes under steam and nitrogen environments reduced the ash contents to 14 and 30 percent respectively. Elemental analysis revealed the presence of a wide distribution of up to 12 elements in all sludge based activated carbons. Equilibrium time for adsorption for sludge based activated carbons was estimated to be 48 hours. Carbonaceous material that was activated under nitrogen environment showed higher adsorption capacity 75mg/g than that activated under steam environment 50mg/g.

Search Terms: sewage sludge, activated carbon adsorbent, lead removal

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## 1. Introduction

The term “heavy metals” is loosely defined and is usually used to indicate metals that have bad effects on people and environment. Heavy metals are metallic elements that have density greater than 5 g/cm<sup>3</sup> [1, 2]. It mainly includes the transition metals, some metalloids, lanthanides and actinides. Some heavy metals are micronutrients e.g. zinc, copper, selenium and iron and are only toxic at high concentrations but other heavy metals including lead, arsenic, cadmium, chromium, nickel and mercury are toxic even at very low concentrations [1].

Heavy metal contamination is one of the more serious environmental problems [3]. The treatment of heavy metals needs special attention because of their persistent and poisonous nature in environment. The heavy metals are part of the earth's crust and are not degradable. Chemical form of heavy metals in water is accessible to living organisms through bioaccumulation in food chain [4]. Heavy metal water pollution is caused by both natural and anthropogenic sources. Natural sources include mobilization of naturally occurring heavy metals from earth crust due to volcanic activity or weathering of rocks from where they are released into water sources [1, 2]. Anthropogenic sources include non-ferrous metal ore mining and smelting, electroplating, industrial activities, organic wastes, refuse burning, transport and power plants [2, 5]. With the rapid boost in industrial growth the discharge of waste water containing heavy metals into the environment is also increasing rapidly. A significant amount of heavy metals is present in atmosphere due to natural and anthropogenic activities from where they reach water bodies by dry deposition and rain [2].

The heavy metals that need particular attention in waste water treatment are zinc, mercury, cadmium, chromium, lead, arsenic, copper and nickel. Arsenic is transported naturally from weathering reactions, biological activity, geochemical reactions, volcanic emissions and anthropogenic activities e.g. mining, burning of fossil fuels, arsenic pesticides and herbicides and use of arsenic additives in livestock [6]. Lead in effluents is generated from mining, painting, batteries etc. Chromium is coming from leather industries, petroleum refineries, chrome-plating, textile industries etc. Sources of cadmium emission are the burning of fossil fuels, smelting and roasting of metal ores, kiln operations, cadmium plating, cadmium alloys,

pigments, Ni-Cd batteries etc. Heavy metals are not degradable so they stick with the environment and tend to build up in living organisms. Heavy metals in contaminated waters get to humans directly or accumulate in vegetation or aquatic life and finally reach humans through the food chain.

Lead can cause serious nervous, intellectual and mental, prenatal and reproductive health, growth, behavior, renal, blood and circulation, bones and muscular, sight, hearing and digestive problems in infants, children and adults. The toxic symptoms are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages [7]. According to the World Health Organization (WHO), the drinking water standard for lead is 0.01 ppm [8].

It is very important to study and develop techniques to remove heavy metals from waters. Research is being done to develop numerous techniques to remove heavy metals from waste water. These methods include chemical precipitation, ion exchange, sorption, membrane filtration, coagulation-flocculation, floatation and electrochemical methods. Sorption is one of the successful and economical techniques for the removal of heavy metals from waste water. The sorption process can generate a high quality effluent and is also reversible. Activated carbon is the most widely used sorbent for waste water treatment. Because of meso-porous and micro-porous structure and high surface area it has high sorption capacity and can be successfully used for sorption of the heavy metals from water. Commercially available activated carbon can be expensive so research is being done to produce activated carbon from cheap and plentiful recourses. The waste materials rich in carbonaceous compounds e.g. agricultural waste, woody waste and municipal waste (tires and sewage sludge) are successfully utilized to produce activated carbon.

Sewage sludge is a waste that is produced in large amounts at waste water treatment plants. Sewage sludge has become an environmental problem because of its production in high amounts throughout the world [8]. Sewage sludge is incinerated or dumped into landfills, land reclamation, agricultural lands and oceans [9]. Incineration is expensive, produces harmful ash contents and air pollution; it is also hampered by bad public image [10]. Landfill is not a sustainable option because it require a lot of space, expensive equipment is needed to control the release of gases and solids, suitable sites for landfills and reclamation are running short due to

urbanization and more stringent environmental rules are applied [9,11]. Use of sewage sludge in agricultural lands increases the risk of soil and ground water contamination with metals [11].

Due to waning and loss of conventional methods of sewage sludge disposal a significant amount of research is going on to find alternative environment friendly and cost effective methods for the reuse of sewage sludge. One alternative is to convert the sewage sludge into sorbents, especially activated carbon because of the presence of carbonaceous compounds [10]. Activated carbon is a highly effective sorbent because of its high surface area and is most commonly used in water and air treatment applications [10, 12].

Activated carbon is produced in two steps, first carbonization of sewage sludge is done and then either physical or chemical activation is carried out. Carbonization is done by heating sewage sludge at high temperature usually from 600 to 800°C under inert environment which removes most of the non-carbon elements in the form of their gaseous products. The carbonaceous material produced after carbonization has surface area around 100m<sup>2</sup>g<sup>-1</sup> [12, 13]. Physical activation is carried out by heating the carbonaceous material at temperature from 800 to 1100°C in oxidizing gas. Controlled burn off of atoms in carbon structure is done and this process also removes the pore blocking materials. Activated carbon obtained after physical activation has surface area about 100-270m<sup>2</sup>g<sup>-1</sup> [13, 14]. Chemical activation is done by mixing carbonaceous material with an activating agent and then heated in inert environment to a sufficiently high temperature so that activating agent reacts with carbonaceous material [10]. Activating agents used by different researchers for chemical activation are KOH, NaOH, H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, and ZnCl<sub>2</sub>. Highest surface area are obtained by chemical activation through KOH activation. Lillo et al. achieved 1882m<sup>2</sup>g<sup>-1</sup> through KOH activation [15].

The main focus of this study is to develop a simplified method to convert sewage sludge into activated carbon for water treatment applications.

## **2. Objectives**

Main objectives of this study are to

1. Produce activated carbon from sewage sludge using a method described in the literature.
2. Design a procedure to produce activated carbon sewage sludge without using an external flowing inert stream.
3. Use the activated carbon to remove lead from water.
4. Compare characteristics and removal efficiency of sewage sludge based activated carbon with commercial activated carbon.

## **3. Theoretical Background Information and Literature Review**

### **3.1. Technologies for treatment of waste water containing heavy metals**

Most commonly used techniques for treatment of waste waters containing heavy metals are chemical, physical, biological and electrochemical. Chemical techniques to remove heavy metals from waste water are chemical precipitation, ion exchange, and sorption. Biological treatment utilizes micro-organisms to remove heavy metals. Physical treatment includes membrane filtration, flotation, coagulation and flocculation. Electrochemical methods involve the plating-out of metal ions on a cathode surface and recovery of metals in the elemental metal state. Electrochemical wastewater technologies involve relatively high investment and expensive electricity supply and so they are not widely adopted [7]. Sorption is now recognized as an effective and efficient technique for removal of heavy metals from waste water. The sorption process can generate a high quality effluent and can be reversed. Sorbents can also be regenerated by using suitable desorption processes.

### **3.2. Sorption**

Sorption is the process in which one substance takes up another substance and holds it. Sorption includes both adsorption and absorption. The sorbing substance is called as sorbate (metal or organic compound) and the solid media that sorbs the sorbate ions or molecules is called a sorbent. The sorption process occurs in following steps



1. Bulk solution transport
2. Film diffusion transport
3. Pore transport
4. Sorption

Sorption includes the attachment of sorbate molecules to the available sorption sites. Sorption can occur on the outer surface of sorbent or in the macropores, mesopores and micropores. The surface area of the outer region of the pellet, macropores and mesopores is very small compared to the surface area of the micropores so sorption occurring on the outer surface, macro and mesopores is considered to be negligible [16].

### 3.3. Sorption Isotherms

The quantity of sorbate that can be sorbed depends on the properties of the sorbate and the temperature. Generally the amount of sorbate being sorbed is determined as a function of concentration at constant temperature. The resulting function is called as sorption isotherm. Experiments to develop sorption isotherms are conducted by using different amounts of sorbent with a fixed initial concentration and volume of sorbate. Most commonly used sorption isotherms are Langmuir sorption isotherm and Freundlich sorption isotherm [16].

#### 3.3.1. Langmuir Sorption Isotherm

Langmuir proposed the theoretical sorption isotherm relating the amount of gas sorbed on a surface to the pressure of the gas or concentration in a solution. The Langmuir sorption isotherm is defined as

$$Q_e = \frac{Q_m K_a C_e}{1 + K_a C_e} \quad (1)$$

where the independent variable  $C_e$  is the equilibrium concentration (mg/L), the response  $Q_e$  is the amount sorbed at equilibrium (mg/g),  $Q_m$  is the monolayer sorption capacity at saturation (mg/g) and  $K_a$  is the equilibrium sorption constant (L/mg).

The Langmuir sorption isotherm assumes: 1) availability of a fixed number of sorption sites; 2) all of the sorption sites have the same energy; 3) sorption is reversible. Equilibrium is attained when the rate of molecules sorbing onto the sorbent

are equal to the rate of molecules desorbing from the surface of the sorbent [17]. The rate of sorption is directly proportional to the difference between the amount sorbed at a particular concentration and the equilibrium amount that can be sorbed at that concentration. At equilibrium this difference is zero [16].

The linear form of the Langmuir sorption isotherm is given below

$$\frac{1}{Q_e} = \frac{1}{K_a Q_m C_e} + \frac{1}{Q_m} \quad (2)$$

The constants in the Langmuir sorption isotherm can be determined by plotting  $1/Q_e$  versus  $1/C_e$  [18].

### 3.3.2. Freundlich Sorption Isotherm

The Freundlich empirical model can be applied to the non-ideal sorption on heterogeneous surfaces and also for multilayer sorption. The Freundlich sorption isotherm is defined as given below

$$Q_e = k_f C_e^{1/n} \quad (3)$$

where the independent variable  $C_e$  is the equilibrium concentration (mg/L), the response  $Q_e$  is the amount adsorbed at equilibrium (mg/g) and  $k_f$  (mg/g) and  $n$  (g/L) are the Freundlich constants related to the sorption capacity and sorption affinity of the sorbent [17].

The linear form of the Freundlich sorption isotherm is given below in which the constants can be determined by plotting  $\log Q_e$  versus  $\log C_e$ .

$$\log Q_e = \log k_f + \frac{1}{n} \log C_e \quad (4)$$

### 3.3.3. Toth Isotherm

The Toth sorption isotherm is a three parameter empirical model and is derived from potential theory. It is useful in describing sorption on heterogeneous surfaces e.g. phenolic compounds on carbon. The Toth isotherm is an improvement over the Langmuir and Freundlich sorption isotherms and is represented as followed

$$Q_e = \frac{K_t C_e}{(a_t + C_e^t)^{1/t}} \quad (5)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount sorbed at equilibrium (mg/g),  $K_t$  is the maximum sorption capacity at saturation (mg/g),  $a_t$  is the sorption equilibrium constant and  $t$  is the model constant known as dissociation parameter and accounts for the sorbent surface heterogeneity [19].

The Toth isotherm is used to describe the sorption of gases when Langmuir isotherm fails to do so. It reduces to the Henry's law at very low surface coverage and reduces to Langmuir isotherm when  $t$  is equal to 1 [17].

### 3.3.4. Langmuir Freundlich Isotherm

The three parameter empirical Langmuir-Freundlich isotherm model is combination of Landmuir sorption isotherm and Freundlich sorption isotherm. This isotherm is very popular as it fits a wide range of equilibrium data especially when Langmuir and Freundlich sorption isotherms do not fit the data [17]. The Langmuir-Freundlich isotherm is defined as followed

$$Q_e = \frac{KQ_{max}C_e^{1/n}}{1+KC_e^{1/n}} \quad (6)$$

where  $C_e$  is the equilibrium concentration (mg/L),  $Q_e$  is the amount sorbed at equilibrium (mg/g),  $Q_{max}$  is the maximum sorption capacity at saturation (mg/g),  $b$  is the constant related to the heat of sorption and  $n$  is the model constant known as heterogeneity parameter.

At low sorbate concentration this isotherm reduces to Freundlich isotherm and does not obey the Henry's law where at high sorbate concentration it determines the monolayer sorption capacity and behaves like Langmuir isotherm [19].

### 3.4. Determining the Parameters of Sorption Isotherms

The parameters for Langmuir and Freundlich isotherms can be found from the linear plots. In order to find the parameters for Toth and Langmuir-Freundlich isotherms non-linear regression is required using e.g. SOLVER in EXCEL. The accuracy of the iterative method used can be determined in terms of the error in the method. Error can be specified as absolute error or relative error. Absolute error is defined as [20]

$$\text{Absolute Error} = \text{Approximate Value} - \text{Exact Value} \quad (7)$$

And relative error is defined as

$$Relative\ Error = \frac{Absolute\ Error}{Exact\ Value} \quad (8)$$

Convergence criteria can be defined in terms of absolute error or relative error. If  $\varepsilon$  is the convergence tolerance, for the absolute error convergence criteria following choices are possible

$$|(\Delta Q_i)_{max}| \leq \varepsilon \quad (9)$$

$$\sum_{i=1}^n |\Delta Q_i| \leq \varepsilon \quad (10)$$

OR

$$[\sum_{i=1}^n (\Delta Q_i)^2]^{1/2} \leq \varepsilon \quad (11)$$

For the relative error criteria following choices are possible

$$\left| \frac{(\Delta Q_i)_{max}}{Q_i} \right| = \varepsilon \quad (12)$$

$$\sum_{i=1}^n \left| \frac{\Delta Q_i}{Q_i} \right| \leq \varepsilon \quad (13)$$

OR

$$\left[ \sum_{i=1}^n \left( \frac{\Delta Q_i}{Q_i} \right)^2 \right]^{1/2} \leq \varepsilon \quad (14)$$

The sum of the squares of the residuals is

$$S_t = \sum_{i=1}^n (y_i - \bar{y})^2 \quad (15)$$

$$S_r = \sum_{i=1}^n e_i^2 = \sum_{i=1}^n (y_i - \hat{y}_{i,model})^2 \quad (16)$$

The goodness of fit is characterized by the correlation coefficient

$$R^2 = \frac{S_t - S_r}{S_t} \quad (17)$$

### 3.5. Sorbents

Different materials used as sorbent in waste water treatment processes are listed below [21].

- Chitosan
- Zeolites
- Clay
- Peat Moss
- Fly Ash
- Coal
- Natural Oxides (Aluminum oxide, Iron oxide)
- Industrial Wastes (Waste slurry, Blast furnace slag, Activated red mud, etc)
- Activated Carbon

### **3.6. Activated carbon**

Activated carbon is the most popular and widely used sorbent in waste water treatment processes throughout the world [21]. Due to well- developed pore structure and large internal surface area, activated carbon has an excellent sorption capacity. Activated carbon is a carbonaceous material with a high degree of porosity and an extended particulate surface area. Activated carbon is prepared from various carbonaceous raw materials. It is prepared by carbonization and activation of carbonaceous substance [22].

### **3.7. Raw Materials for Activated Carbon**

Due to the increase in the use of activated carbons in adsorption applications, their costs are getting relatively expensive mainly owed to the reduction in the natural resources of raw materials used to produce activated carbons. There are several researches to produce activated carbon from cheap and abundant sources. Carbonaceous materials are found to be a substitute to produce activated carbon. Agricultural by-products, for example, nuts and stones of fruits like walnuts, peanuts, olives, dates, almonds and apricot are being used to produce activated carbon. Similarly waste products from cereal manufacturing such as rice, coffee, soybean, maize and corn; also many seed wastes like olive cakes, sugar canes and oil palm shells also being used to produce activated carbon [23]. Kongsuwan et al. successfully used activated carbon produced from eucalyptus bark for the removal of copper and lead ions [24]. Coffee residue collected from coffee houses was used to produce activated carbon by chemical activation with zinc chloride [25]. Similarly Tunisian

olive cakes, i.e. a byproduct from olive oil mill were used to produce activated carbon by chemical activation with phosphoric acid [26]. Amuda et al. studied the successful use of activated carbon to remove zinc ions from waste water produced from coconut shells [27]. Sorption capacity and efficiency of activated carbon produced from different raw materials is given in Table 1.

Sewage sludge is a waste that is produced in large amounts at sewage treatment plants. For example, more than 10 million tons dry sludge-based matter is generated per year in Europe from waste water treatment plants. Sewage sludge is not best suited to be used as fertilizer because of its Eco toxicological effects on soils [28], so the disposal and use of sewage sludge can be a big problem. An alternative use of sewage sludge is to convert it into adsorbents due to the presence of carbonaceous materials.

### 3.8. Production of Activated Carbon from Sewage Sludge

Researchers have shown that high surface area adsorbents can be produced from sewage sludge. Main steps in production of activated carbon from sewage sludge are carbonization and activation. Schematic diagram for the production of activated carbon from sewage sludge is given in Figure 1.

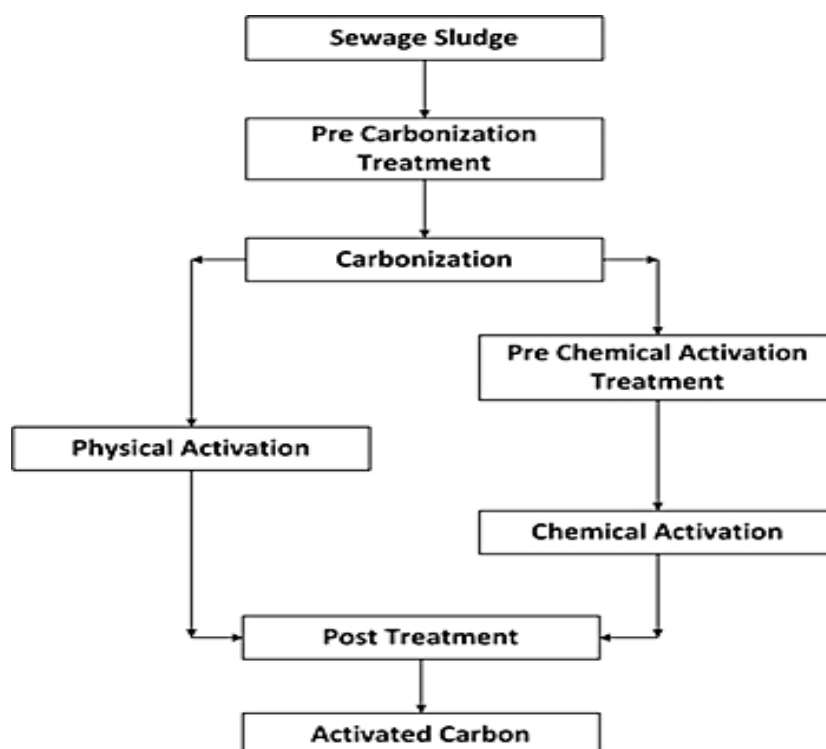


Figure 1: Schematic flow chart for the production of activated carbon

Table 1: A literature review summary on heavy metals removal using activated carbon of different sources

Author	Ref.	Activated Carbon	Carbonization		Activation Method			Metals Removed	Initial Conc. (mg/L)	Sorption Capacity (mg/g)	Final Conc. (mg/L)	Efficiency (%)	
			Temp. (°C)	Time (hr)	Reagent	Temp. (°C)	Time (hr)						
Tian Gan et al. (2008)	[29]	Commercial AC			30% H <sub>2</sub> O <sub>2</sub>			Pb	30	37.922		55	
Corapcioglu et al. (1987)	[30]	Hydrous AC						Cu, Pb, Ni, Zn				100	
Jusoh et al. (2007)	[31]	Granular AC						Pb	20.17		0.098	99.97	
								Cd	20.54		0.004	99.51	
Vinay et al. (2008)	[32]	AC-Zeolite composite			NaOH	700		Ni	17.6-586.9	70.43			
								Cu	19-635.4	109.29			
								Cd	33.7-1124	161.87			
								Pb	62.1-2072	549.08			
Kang et al. (2008)	[33]	AC Fiber			KOH	Boiling	3	Cu		94.5			
		Granular AC			KOH	Boiling	3			49.5			
										Cd			32.8
													10.3
Nadeem et al. (2006)	[18]	AC from pods of M. Oleifera	800	0.5	HCl	Room Temp.	4	Pb	30	29.08		96.58	
Goel et al. (2005)	[34]	Coconut shells AC			Na <sub>2</sub> S	Room Temp.	24	Pb	6	2.89		100	
Yousef et al. (2004)	[35]	Corn Stalks AC	600		H <sub>2</sub> SO <sub>4</sub>	220	1	Cd	85.43	38.22	2.25	97.37	
					ZnCl <sub>2</sub>	Room Temp.	72			31.47	5.62	93.42	

(Table continues)

Author	Ref.	Activated Carbon	Carbonization		Activation Method			Metals Removed	Initial Conc. (mg/L)	Sorption Capacity (mg/g)	Final Conc. (mg/L)	Efficiency (%)
			Temp. (°C)	Time (hr)	Reagent	Temp. (°C)	Time (hr)					
Kongsuwan et al. (2009)	[24]	AC from Eucalyptus			H <sub>3</sub> PO <sub>4</sub>			Cu		28.59		
								Pb		109.82		
Boudrahem et al. (2009)	[25]	AC from Coffee residue	600	1	ZnCl <sub>2</sub>	85	7	Pb	10	9.647		100
Baccar et al. (2009)	[26]	AC from Olive Cake	650	2	H <sub>3</sub> PO <sub>4</sub>	104	2	Cu	470	12		
Issabayeva et al. (2006)	[36]	Commercial AC Palm shell						Pb	10	95.2		
Garcia et al. (2003)	[37]	Commercial Merck Carbon			SO <sub>2</sub>	900		Cd	67.45	51.48	8.99	86.67
Rao et al. (2006)	[38]	AC (cieba pentandra hulls)	200	2	Steam Activation			Cu	80	28.8	8	90
								Cd		19.5	9.6	88
Yanagisawa et al. (2010)	[39]	Mg and AC composite			Mg	380	4	Zn		9.67		
								Cd		10.56		
Ahn et al. (2009)	[40]	Granular AC			Anionic Surfactants	20	4	Cd	100	22.25		100
Liu et al. (2007)	[41]	Coconut shell AC			HNO <sub>3</sub>	90	12	Cr	50	13.89		100
					NaOH	30	48					
Natali et al. (2007)	[42]	Granular AC			Steam Activation			Cr		7		



### 3.8.1. Pre Carbonization Treatment

The sewage sludge is first pre-carbonized. Pre-carbonization treatment is done by impregnating the sewage sludge with a chemical reagent e.g. KOH, H<sub>2</sub>SO<sub>4</sub>, ZnCl<sub>2</sub>, etc. These chemical reagents act as dehydrating agent and oxidants that influence decomposition during carbonization and prevent the formation of tar and enhance the formation of carbon.

A few studies that used pre-carbonization on sewage sludge are listed in Table 2, along with resulting surface areas. Wang et al. carried out the pre carbonization treatment. The sewage sludge sample was first centrifuged and dried at 105 °C under vacuum until constant weight. The dried sewage sludge was impregnated with 3M KOH for 24 hr at room temperature and then it was dried again at 105 °C [43]. Rio et al. performed the pre carbonization treatment with sulfuric acid. Dried sewage sludge was impregnated with 3 M H<sub>2</sub>SO<sub>4</sub> for 6 hr. The resulting mixture was filtered and dried at 105 °C [44]. Lu et al. started the pre carbonization treatment by first drying the sewage sludge at 108 °C for about 24 hr. Dried sewage sludge was soaked in 5 M ZnCl<sub>2</sub>, stirred well mixed and left to stand for 24 hr, then filtered and dried at 108 °C in the drying oven [9].

Table 2: Surface areas obtained with pre carbonization treatment

Author	Pre Carbonization Treatment				Surface Area (m <sup>2</sup> /g)
	Reagent	Conc. (M)	Temp. (°C)	Time (hr)	
Wang et al. (2008)	KOH	3	Room Temp.	24	381.62
Rio et al (2005)	H <sub>2</sub> SO <sub>4</sub>	3	Room Temp.	6	377
Lu et al. (1996)	ZnCl <sub>2</sub>	5	Room Temp.	24	309

### 3.8.2. Carbonization

Carbonization comprises heating the carbonaceous raw material to temperatures typically in the range of 500–800 °C under an inert atmosphere. The induced thermal decomposition of the material eliminates most of the non-carbon elements (hydrogen, oxygen, etc.) through their release as gaseous volatile products and this creates the grapheme layers.

Mendez et al. carried out the carbonization of sewage sludge at 450 °C in a vertical electric furnace. Ten grams of sample was placed in a glass reactor in the middle of the electric furnace and heated at 10°C/min up to 450 °C. Maximum temperature of 450 °C was maintained for 1 hr in nitrogen environment. Nitrogen flow rate of 150 mL/min was used during all the experiment [12]. Seredych et al. produced carbon from dewatered sewage sludge taken from Wards Island Water Pollution Control Plant. First the sewage sludge was dried at 120 °C for 48 h then it was carbonized at two different temperatures 650 °C and 950 °C in nitrogen environment in a fixed-bed horizontal furnace. The heating rate was 10 °C/min and the holding time for maximum temperature was 0.5 hr [13]. The Surface area obtained after carbonization in these two studies is given in Table 3.

Table 3: Surface Area obtained after Carbonization

Author	Temperature (°C)	Time (hr)	Atmosphere	Surface Area (m <sup>2</sup> )
Mendez et al. (2005)	450	4	N <sub>2</sub>	81
Seredych et al. (2006)	650	0.5	N <sub>2</sub>	93
Seredych et al. (2006)	950	0.5	N <sub>2</sub>	103

### 3.8.3. Activation

Carbonization is usually followed by activation to create the porous structure. The activation process increases the sorption capacity by increasing the internal surface area to a large extent [21]. Many activation techniques are developed and can be divided into two categories: 1) physical activation and 2) chemical activation.

#### 3.8.3.a. Physical activation

Physical activation is based on the reaction of various forms of carbonaceous raw material at elevated temperatures with steam, carbon dioxide, carbon monoxide, or oxygen.. This removes the pore blocking substances and increases the surface area of carbon.

Mendez et al. performed physical activation as follows. After carbonization, the carbonaceous raw material was placed in a glass reactor and heated at 10 °C/min

up to 275 °C. Maximum temperature was maintained for 4 hr. The oxygen flow rate used during the physical activation was 5 mL/min and total flow rate was 150 mL/min of N<sub>2</sub>/O<sub>2</sub> [12]. Ros et al. produced activated carbon through physical activation is described as follows. The sewage sludge sample was first dried at 105 °C for 48 h. Carbonization was done in a tubular furnace in nitrogen environment. Maximum temperature for carbonization was up to 700 °C maintained for 0.5 hr. Then, the samples were allowed to cool down to room temperature in nitrogen environment. Heating rate to reach maximum temperature was 15 °C/min. Physical activation experiment was carried out with 4 g precursor. The carbonized material was placed in a horizontal furnace and the furnace was purged with nitrogen for 10-20 min prior to physical activation. The sample was heated to 800 °C at a heating rate of 5 °C/min under flowing nitrogen. After reaching the maximum temperature nitrogen flow was switched to CO<sub>2</sub> at a flow rate 100 ml/min. The maximum temperature and CO<sub>2</sub> flow rate was maintained for the 4 hr. After completion of physical activation time period the sample was cooled down under nitrogen at a flow rate of 100 ml/min. As a last step the activated carbon was washed with HCl. Final acid washing decreases the ash contents and increases the surface area [14]. Surface area obtained after physical activation process is given in Table 4.

Table 4: Surface area after Physical Activation

Author		Temp. Rate (°C/min)	Temp. (°C)	Time (hr)	Atmosphere	Surface Area (m <sup>2</sup> /g)
Mendez et al. (2005)	<b>Carbonization</b>	10	270	4	Air	105
Ros et al. (2006)		5	800	4	CO <sub>2</sub>	269

### 3.8.3.b. Chemical Activation

Chemical activation of the surface of activated carbon with oxidizing agents such as KOH and H<sub>2</sub>SO<sub>4</sub> is done to improve its adsorption capacity. The chemical activation process increases the numbers and dimensions of pores and increases the internal surface area to a large extent. Chemical activation is done in two steps, i.e. pre chemical activation treatment followed by chemical activation.

Pre chemical activation treatment comprises of impregnation of carbonaceous material with chemical reagent. Lillo et al. carried out pre chemical activation by impregnating carbonaceous material with KOH in 1/1 weight ratio at 80 °C for 2 hr [15]. Ros et al. performed the pre chemical activation with KOH and NaOH. Carbonaceous material was mixed with activating reagent at 60 °C for 2 hr. After impregnation material was filtered and dried at 110 °C [18]. Shen et al. impregnated the carbonaceous material with KOH at a weight ratio of 1/1. Material was mixed for 4hr at a temperature of 120 °C [45].

Chemical activation is done by heating the impregnated carbonaceous material at 600 °C to 900 °C in an inert environment. Lillo et al. performed chemical activation by heating the impregnated mixture up to 700 °C, using 5 °C/min heating rate in a horizontal furnace in nitrogen atmosphere with a flow rate of 500 mL/min of nitrogen. Dwell time for the maximum temperature was one hour [15]. Ros et al. carried out the chemical activation step by heating impregnated carbonaceous material up to 700 °C, at a heating rate of 5 °C/min in inert nitrogen environment. The maximum temperature was maintained for 1 hr and nitrogen flow rate was maintained at 100 mL/min [14]. Shen et al. took the impregnated mixture and heated it in a furnace to a maximum temperature of 850 °C; approaching the maximum temperature at a temperature rate of 6 °C/min. Maximum temperature was maintained for an hour. Activation was carried out in nitrogen environment with 36 mL/min nitrogen flow rate [45]. Surface area obtained after chemical activation step is given in Table 5.

Table 5: Surface Area obtained after Chemical Activation

Author	Activation Conditions				Surface Area
	Temp. Rate (°C/min)	Temp. (°C)	Time (hr)	Atmosphere	m <sup>2</sup> /g
Lillo et al. (2008)	5	700	1	N <sub>2</sub>	1301
Ros et al. (2006)	5	700	1	N <sub>2</sub>	1686
	5	700	1	N <sub>2</sub>	1224
Shen et al. (2006)	-	850	1	N <sub>2</sub>	658

#### **3.8.4. Post Activation Treatment**

Acid washing of activated carbon is done to remove the remaining activating agent and reduce the ash contents. Mostly HCl is used for acid washing of activated carbon. After washing with acid, the activated carbon is rinsed with distilled water to raise the pH to 7. Hwang et al. [8] used 1M HCl for post treatment. Ros et al. [14] and Lillo et al. [15] used 5M HCl to wash the activated carbon.

#### **3.9. Removal of Heavy Metals using Sewage Sludge based Activated Carbon**

Activated carbon is the most widely used sorbent in removal of heavy metals from water but it is expensive. Searching for low cost and readily available sorbent is one of the main focuses of research these days. As sewage sludge is available everywhere in the world, so many people have studied the removal of heavy metals from water using activated carbon produced from sewage sludge. Rio et al. used successfully the activated carbon produced from sewage sludge to remove copper ions from water and reported 84 mg/g sorption capacity [44]. Rozada et al. used activated carbon produced from sewage sludge to remove mercury, lead, copper and chromium ions from water and found it successful [46]. Seredych et al. studied the removal of copper ions from water using sewage sludge based activated carbon and reported a sorption capacity of 63.48 mg/g [13]. Zhai et al. removed cadmium and nickel ions from water utilizing activated carbon produced from sewage sludge and reported sorption capacity to be 16.7 and 9.09 mg/g respectively [47]. Zhang et al. applied activated carbon produced from sewage sludge to remove mercury from water and found it successful [48]. Mendez et al. used sewage sludge based activated carbon to remove iron ions from water and reported the removal efficiency to be 99.7% [12]. Gasco et al. study the desalination of water using activated carbon produced from sewage sludge and removed sodium, potassium, calcium and magnesium ions successfully from water [11].

Studies carried out by researchers to produce activated carbon from sewage sludge and its use in removal of heavy metals from water are listed in table 6 to 8.

Table 6: Pre-carbonization treatment and carbonization conditions

Author	Ref.	Sludge Type	ID	Pre Carbonization Treatment					Carbonization Conditions			
				Reagent	Conc. (M)	Reagent-Sludge Weight Ratio	Time (hr)	Temp. (°C)	Temp. Rate (°C/min)	Temp. (°C)	Time (hr)	Atmosphere
Gasco et al. (2005)	[11]	Sewage Sludge		H <sub>2</sub> SO <sub>4</sub>		1:1	24	105	3	450	1	Air
Hwang et al. (2008)	[8]	Sewage Sludge	Hwang-1						10	700	0.5	N <sub>2</sub>
			Hwang-2									
Lillo et al. (2008)	[15]	Sewage Sludge							15	700	0.5	N <sub>2</sub>
Lu et al. (1996)	[9]	Sewage Sludge		ZnCl <sub>2</sub>	5		24	25	20	650	2	N <sub>2</sub>
Mendez et al. (2005)	[12]	Sewage Sludge							10	450	1	N <sub>2</sub>
Rio et al. (2005)	[44]	Sewage Sludge		H <sub>2</sub> SO <sub>4</sub>	3	1.5:1	6	25	20	700	3.67	N <sub>2</sub>
Ros et al. (2006)	[14]	Sewage Sludge	Ros-1									
			Ros-2									
			Ros-3									
			Ros-4									
Rozada et al. (2008)	[46]	Sewage Sludge	Rozada-1	H <sub>2</sub> SO <sub>4</sub>	18.4	1:1	48	25	40	650	0.5	N <sub>2</sub>
			Rozada-2	ZnCl <sub>2</sub>		1:1	48	25	5	650	0.09	N <sub>2</sub>
Shen et al. (2007)	[45]	Sewage Sludge							5	400	0.67	N <sub>2</sub>
Seredych et al. (2006)	[13]	Sewage sludge							10	650	0.5	N <sub>2</sub>
Wang et al. (2008)	[43]	Sewage Sludge		KOH	3		24	25	40	600	1	Steam
Zhai et al. (2004)	[47]	Sewage Sludge		ZnCl <sub>2</sub>			24			850		N <sub>2</sub>
Zhang et al. (2005)	[48]	Sewage Sludge	Zhang-1	H <sub>2</sub> SO <sub>4</sub>	3		24	105	10	650	1	N <sub>2</sub>
			Zhang-2	H <sub>3</sub> PO <sub>4</sub>	3		24	105	10	650	1	N <sub>2</sub>
			Zhang-3	ZnCl <sub>2</sub>	5		24	105	10	650	1	N <sub>2</sub>

Table 7: Pre-activation treatment and carbonization conditions

Author	ID	Pre Activation Treatment					Activation Conditions			
		Reagent	Conc. (M)	Reagent-Sludge Weight Ratio	Time (hr)	Temp. (°C)	Temp. Rate (°C/min)	Temp. (°C)	Time (hr)	Atmosphere
Gasco et al. (2005)										
Hwang et al. (2008)	Hwang-1	KOH			2	80	10	800	1.5	N <sub>2</sub>
	Hwang-2	NaOH	1.25		2	80	10	850	1.5	N <sub>2</sub>
Lillo et al. (2008)		KOH		1:1			5	700	1	N <sub>2</sub>
Lu et al. (1996)										
Mendez et al. (2005)							10	270	4	Air
Rio et al. (2005)										
Ros et al. (2006)	Ros-1						5	800	4	CO <sub>2</sub>
	Ros-2	H <sub>3</sub> PO <sub>4</sub>		3:1	2	85	5	450	4	N <sub>2</sub>
	Ros-3	NaOH		3:1	2	60	5	700	1	N <sub>2</sub>
	Ros-4	KOH		3:1	2	60	5	700	1	N <sub>2</sub>
Rozada et al. (2008)	Rozada-1									
	Rozada-2									
Shen et al. (2007)		KOH		1:1	4	120	6	850	1	N <sub>2</sub>
Seredych et al. (2006)										
Wang et al. (2008)										
Zhai et al. (2004)										
Zhang et al. (2005)	Zhang-1									
	Zhang-2									
	Zhang-3									

Table 8: Post treatment, surface area and removal of heavy metals using sludge based activated carbon

Author	ID	Post Treatment			Surface Area (m <sup>2</sup> /g)	Metals Removed	Initial Conc. (mg/L)	Adsorption Capacity (mg/g)	Final Conc. (mg/L)	Efficiency (%)
		Reagent	Conc. (M)	Time (hr)						
Gasco et al. (2005)					400	Na	10500			69.66-76.78
						K	380			57.80-66.00
						Ca	400			42.85-44.84
						Mg	1350			12.38-35.12
Hwang et al. (2008)	Hwang-1	HCl	1	2	450	I <sub>2</sub>		465.83		
	Hwang-2	HCl	1	2	422	I <sub>2</sub>		410.61		
Lillo et al. (2008)		HCl	5		1301					
Lu et al. (1996)					309					
Mendez et al. (2005)					105	Fe	100			99.7
Rio et al. (2005)					377	Cu	100			84
Ros et al. (2006)	Ros-1				269					
	Ros-2	D-water			17					
	Ros-3	HCl	5		1224					
	Ros-4	HCl	5		1686					
Rozada et al. (2008)	Rozada-1	HCl	3		216	Hg	10-1000	175.2		
						Pb	10-1000	64.1		
	Rozada-2	HCl	3		472	Cu	10-1000	30.7		
						Cr	10-1000	15.6		
Shen et al. (2007)		HNO <sub>3</sub>			658					
Seredych et al. (2006)					93	Cu	10-1000	63.48		
Wang et al. (2008)		D-water			381.62	Dye	300		9	97
Zhai et al. (2004)		HCl		24	555	Cd	40	16.7	12	70
						Ni	30	9.09	9	70
Zhang et al. (2005)	Zhang-1	NaOH	1		408	Hg	200	25*		
	Zhang-2	NaOH	1		289		200	33*		
	Zhang-3	HCl	1		550		200	50*		

\* 8, 6 and 4 g of activated carbon were enough to remove all mercury in the 200 mg/L solutions respectively.



## 4. Apparatus

The activated carbon from sewage sludge has been produced by carbonization and activation. The apparatus is designed to perform these two processes with/without nitrogen gas as shown in Fig.1. Nitrogen gas is supplied from the nitrogen cylinder through a needle valve and a check valve. Needle valve is installed to make fine adjustment in flow of nitrogen and check valve is installed to avoid any backward flow of gases. Sewage sludge is charged into the steal boat and placed into the steal chamber which is in turn placed into the muffle furnace at high temperature. Steal chamber is an air tight horizontal cylindrical chamber with an inlet and an outlet connection for the flow of the gases. In order to find the temperature inside the chamber, a thermocouple is inserted from the exit line, into the chamber. In the exit line, a tar trap is installed to collect the tar produced during the carbonization process. A check valve is installed after the tar trap to avoid backward flow of gases. In order to measure the nitrogen flow rate, a gas burette is installed in the exit line.

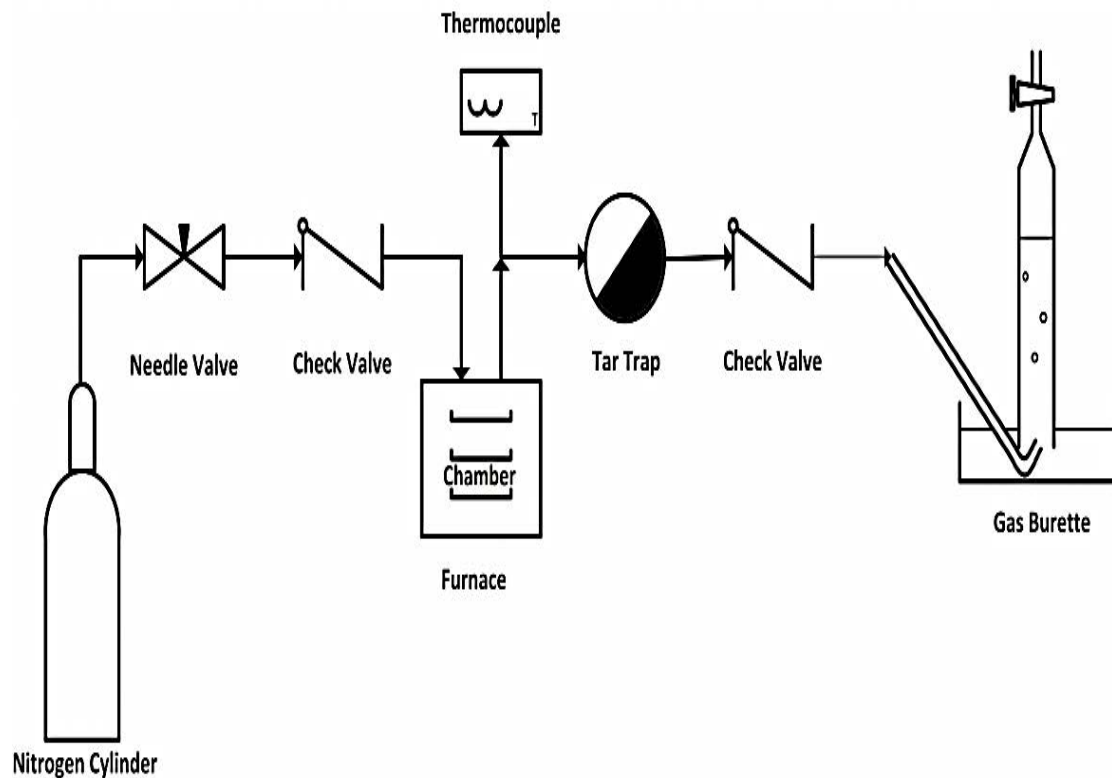


Figure 2: Schematic experimental setup for conversion of sewage sludge to activated carbon

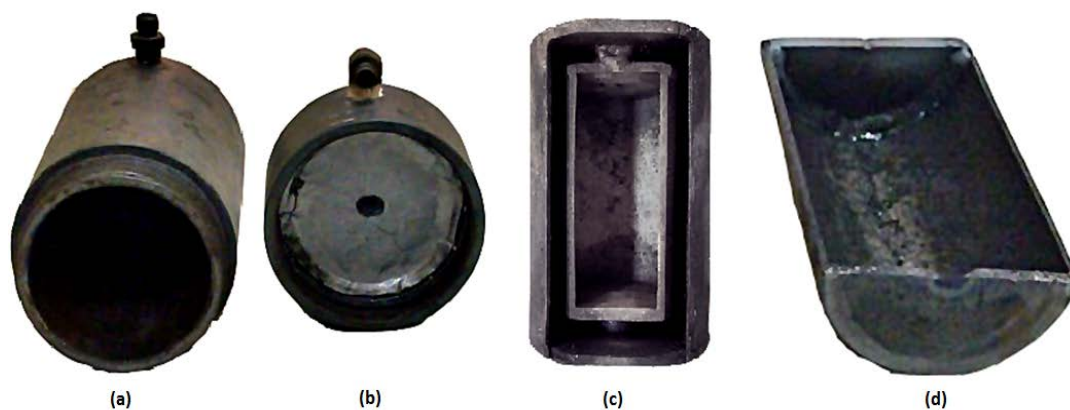


Figure 3: (a) Steel Chamber, (b) Lid, (c) Steel crucible for steam carbonization / activation, (d) Steel crucible for nitrogen carbonization / activation

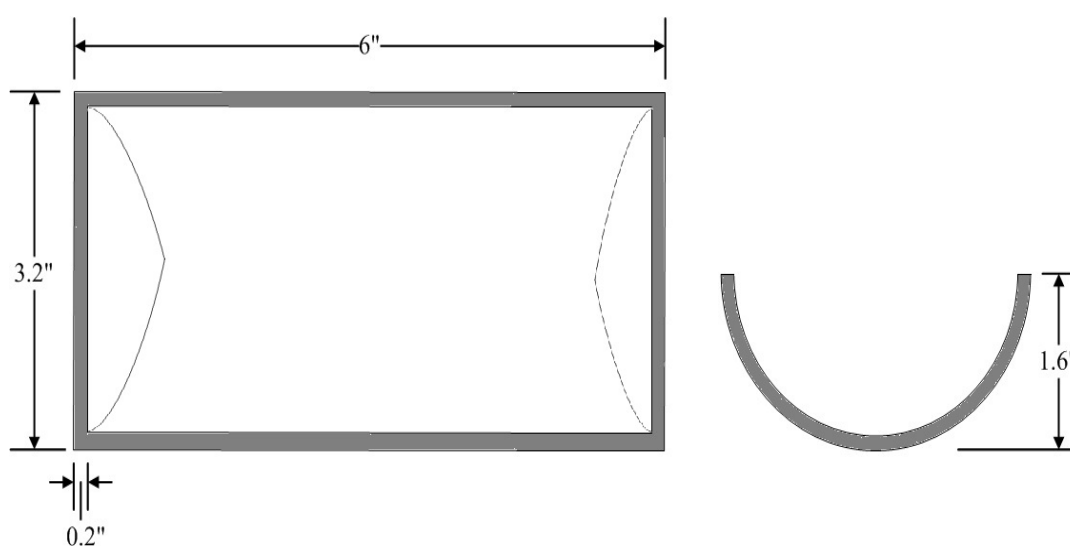


Figure 4: Boat for carbonization and activation under nitrogen environment

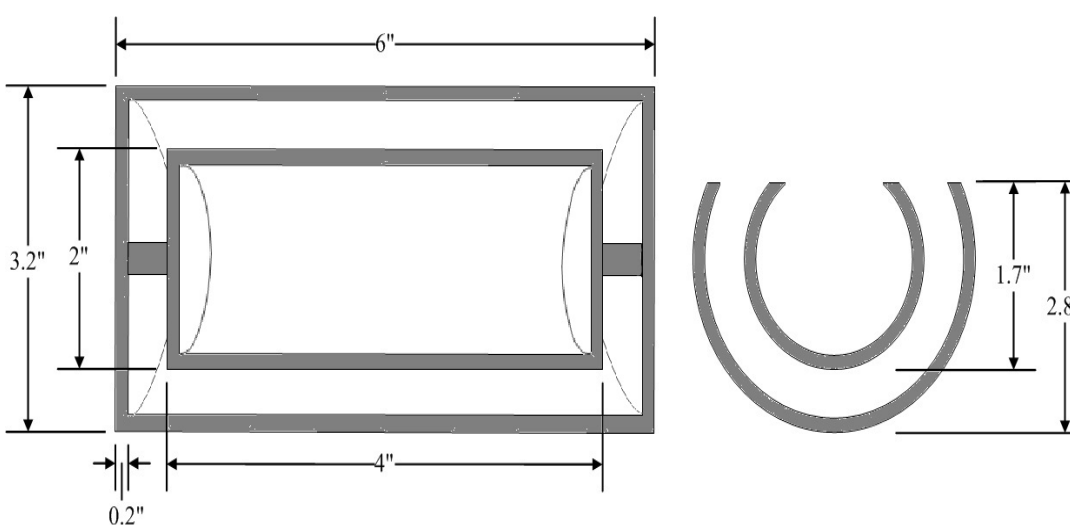


Figure 5: Boat for carbonization and activation under steam environment

## **5. Materials**

Dewatered sewage sludge was taken from waste water treatment plant in Sharjah UAE. The following reagents were used such as hydrochloric acid, nitric acid (MERCK), potassium hydroxide pellets (MERCK), sodium hydroxide pellets (Riedel-de Haën), lead nitrate pellets (HIMEDIA), commercial activated carbon (NORIT 100-400mesh, Sigma Aldrich) and nitrogen gas (99.95% purity).

## **6. Methods**

### **6.1. Preparation of Activated Carbon**

#### **6.1.1. Carbonization**

Sewage sludge was dried under the sunlight for a week. Carbonization was done in two ways, one with nitrogen and second without nitrogen. For carbonization with nitrogen dried sewage sludge was weighed and placed inside the steel boat which was placed inside the chamber. Sewage sludge was heated at a rate of 5°C/min in the furnace until a maximum temperature of 700°C was reached. Maximum temperature was maintained for half an hour. A nitrogen flow of 3 ml/s was maintained during this process. Carbonaceous material was taken out of the steel boat and was ground to a particle size < 212 micron. The carbonaceous material obtained was termed as N.

For carbonization without nitrogen dried sewage sludge was weighed and placed into the steel boat designed for this process. Water was added to the water side of boat and placed inside the chamber. Sewage sludge was heated at a rate of 5°C/min in furnace until a maximum temperature of 700°C was reached. Maximum temperature was maintained for half an hour. Carbonaceous material was taken out of the steel boat and was ground to a particle size < 212 micron. The carbonaceous material obtained was termed as S.

#### **6.1.2. Activation**

N-carbonaceous material was mixed with KOH in a 3 KOH to 1 carbonaceous material weight ratio, 20ml of distilled water was added and was then heated at a temperature rate of 5°C/min to a maximum temperature of 700°C. Maximum temperature was maintained for one hour. A nitrogen flow of 3 ml/s was maintained

during this process. Then the furnace was switched off and allowed to be cooled down overnight. The activated carbon obtained was termed as NN.

Activation of the S-carbonaceous material was done in two ways. First the S-carbonaceous material was impregnated with 3 molar KOH solution for 2 hours at room temperature. Then it was filtered and was heated inside the furnace at a temperature rate of 5°C/min. A maximum temperature of 700°C was maintained for one hour, after that the material was allowed to be cooled down overnight. The activated carbon obtained was termed as SIS. Second, S-carbonaceous material was mixed with KOH in a 3 KOH to 1 carbonaceous material weight ratio, placed inside the steel boat and 20ml of distilled water was added. Distilled water was added to the water side of steel boat. The mixture was heated at a temperature rate of 5°C/min to a maximum temperature of 700°C and the maximum temperature was maintained for one hour. The activated carbon obtained was termed as SS.

### **6.1.3. Post Activation Treatment**

NN activated carbon was washed with 5 molar HCl to remove the ash contents and the remaining of the activation agent. Then it was rinsed with the distilled water to remove the chloride ions until a pH of 6 was reached for the washing water.

Post activation of SS activated carbon was done in three different ways 1.) The post treatment for the SS activated carbon was carried out similarly as for the NN activated carbon 2.) SS activated carbon was washed with 5 molar HNO<sub>3</sub> thoroughly and then rinsed with distilled water until a pH of 6 was achieved for the washing water and was termed as SS<sub>NO3</sub> 3.) Soxhlet was used to wash the activated carbon. Distilled water in the flask was changed after each 24 hour period and the pH was measured. Operation was continued until the pH of the washing distilled was constant and the product was termed as SS<sub>sox</sub>.

## **6.2. Surface Characterization**

### **6.2.1. Sorption of Nitrogen**

ASAP 2010 (Micromeritics) was used to measure the nitrogen isotherms at a temperature of 77 K. Before the experiment, the samples were heated at a temperature of 393 K and then outgassed under a vacuum of 10<sup>-5</sup> torr to constant pressure. Characterization of pore sizes and pore structure were accomplished using Density Functional Theory (DFT) [58]. DFT works under the assumption that the

experimental isotherm can be expressed as the sum of the convolution of a kernel function which represents the isotherm of an ideal homoporous sorbent with a frequency distribution of the pore sizes. The convolution is done by fitting the experimental isotherms into combinations of pre-existing isotherms for various pore sizes until the best fit is obtained. DFT provides an accurate method of describing inhomogeneous system like activated carbons. Using DFT, specific surface area ( $S_{DFT}$ ), total pore volume ( $V_t$ ), micropore volume ( $V_{mic}$ ), volume of pores less than 10 Å ( $V_{<10Å}$ ) were calculated [58]. These data was used to calculate the average pore size ( $L$ ). Moreover, the surface areas, SBET, were also calculated using BET method.

#### **6.2.2. Boehm Titration**

The amount of oxygenated surface groups was determined using Boehm titration method. One gram of activated carbon was added to 50ml of 0.05M solutions of NaOH, and HCl. The samples were sealed and agitated by shaking for 24 hours and filtered. 10ml of each filtrate was pipetted and excess of acid or base was titrated 0.05M NaOH or HCl solution depending on the original titrant used. End point was determined by using phenolphthalein indicator for acid titrated with base and methyl blue for base titrated with acid. The amount of acidic sites of various types was calculated under the assumption that NaOH neutralizes carboxylic, phenolic, and lactonic groups. The number of surface basic sites was calculated from the amount of hydrochloric acid that reacted with the carbon [49, 50, 51].

#### **6.2.3. pH Measurement**

0.4 g of dry carbon powder was added to 20 ml of water and the suspension was stirred overnight to reach equilibrium. Then the samples were filtered and the pH of the filtrates was measured [52].

#### **6.2.4. Thermal Analysis**

PerkinElmer thermal analyzer was used to carry out thermal analysis. The instrument settings were: heating rate 10°C/min, nitrogen atmosphere with flow rate of 100 mL/min. Approximately 10 to 15 mg of a ground carbon sample was used for each measurement. Thermo gravimetric (TG) and Differential thermo gravimetric (DTG) curves were obtained. TG curves provide the % weight loss caused by the decomposition of surface functional groups as a result of heating. DTG curves are

obtained from TG curves. The position of the peaks on DTG curves is related to the thermal stability of the surface groups [53].

#### **6.2.5. Ash Content**

TA instrument thermal analyzer was used to determine the ash content in the carbon samples. 10 to 15 mg sample of the carbon was placed in a platinum pan. The temperature was then ramped in nitrogen atmosphere at a temperature rate of 10°C per minute from ambient to 650°C. It was held isothermal at 650°C for 20 minutes then ramped to 655°C at which the flow gas was then switched to air. The temperature was then ramped in air at a temperature rate of 10°C per minute to 800°C.

#### **6.2.1. SEM/EDS Mapping and Elemental Analysis**

The samples were analyzed using scanning electron microscope (SEM, JEOL 5910LV) equipped with an energy dispersive X-ray spectrometer (EDAX Apollo silicon drift system). SEM was used to study the chemical and the structural heterogeneity of the activated carbon surface by collecting magnified images of the surface. EDS mapping was used for the elemental analysis of the activated carbons surface and to investigate the level of surface heterogeneity and contamination. To avoid surface charging the material was coated with carbon. The SEM was operated at an accelerating voltage of 15 and 20 keV. SEM and EDS analysis were done on the same samples of activated carbons. SEM (Philips XL 30 SEM) was used to take the micrographs of SS and NN activated carbons before and after the adsorption experiments.

### **6.3. Adsorption Study**

A stock solution of lead was prepared of a 1000 ppm concentration and the pH was adjusted between 4 to 5 using HNO<sub>3</sub>.

To find the equilibrium time for activated carbon, four sets of two 100ml solutions of 10ppm and 100ppm concentration were prepared. Solutions were taken into 250ml conical flasks and 0.2g of activated carbon was added to all. The solutions with activated carbon were placed in the mechanical shaker and stirred at a rate of 250 oscillations/min. One set of solutions was removed from the shaker after each 24 hours, filtered and lead concentration was analyzed using atomic absorption spectrometer until the final concentration of lead ions in the solutions was constant.

In order to produce sorption isotherms of activated carbons, 6 solutions (100ml) were made having the following concentrations: 5, 10, 50, 100, 200, and 400ppm. The pH of the solutions was adjusted to approximately 5 before adding 0.5g of activated carbon. All solutions were placed in the mechanical shaker and stirred at a rate of 250 oscillations/min. After 48 hours solutions were removed from shaker, filtered and analyzed for lead concentration using atomic absorption spectrometer. Final pH of the solutions was measured.

## 7. Results and Discussion

Eight samples of activated carbon were characterized during various stages of preparation. The details of the production of these samples are given in Table 9 and illustrated in Figure 6.

Table 9: Details of the production of the activated carbons and carbonaceous materials which are investigated

Sample ID	Carbonization	Pre-Activation Treatment	Activation	Post Activation Treatment
S	Steam	-	-	-
SS	Steam	Physical Mixing KOH:AC 3:1	Steam	5 M HCl
SS <sub>NO3</sub>	Steam	Physical Mixing KOH:AC 3:1	Steam	5 M HNO <sub>3</sub>
SS <sub>sox</sub>	Steam	Physical Mixing KOH:AC 3:1	Steam	Rinsed in Soxhlet
N	Nitrogen	-	-	-
NN	Nitrogen	Physical Mixing KOH:AC 3:1	Nitrogen	5 M HCl
SN	Steam	Physical Mixing KOH:AC 3:1	Nitrogen	5 M HCl
CAC	Norit Commercial AC Product No. C3445 with 100-400 mesh size			

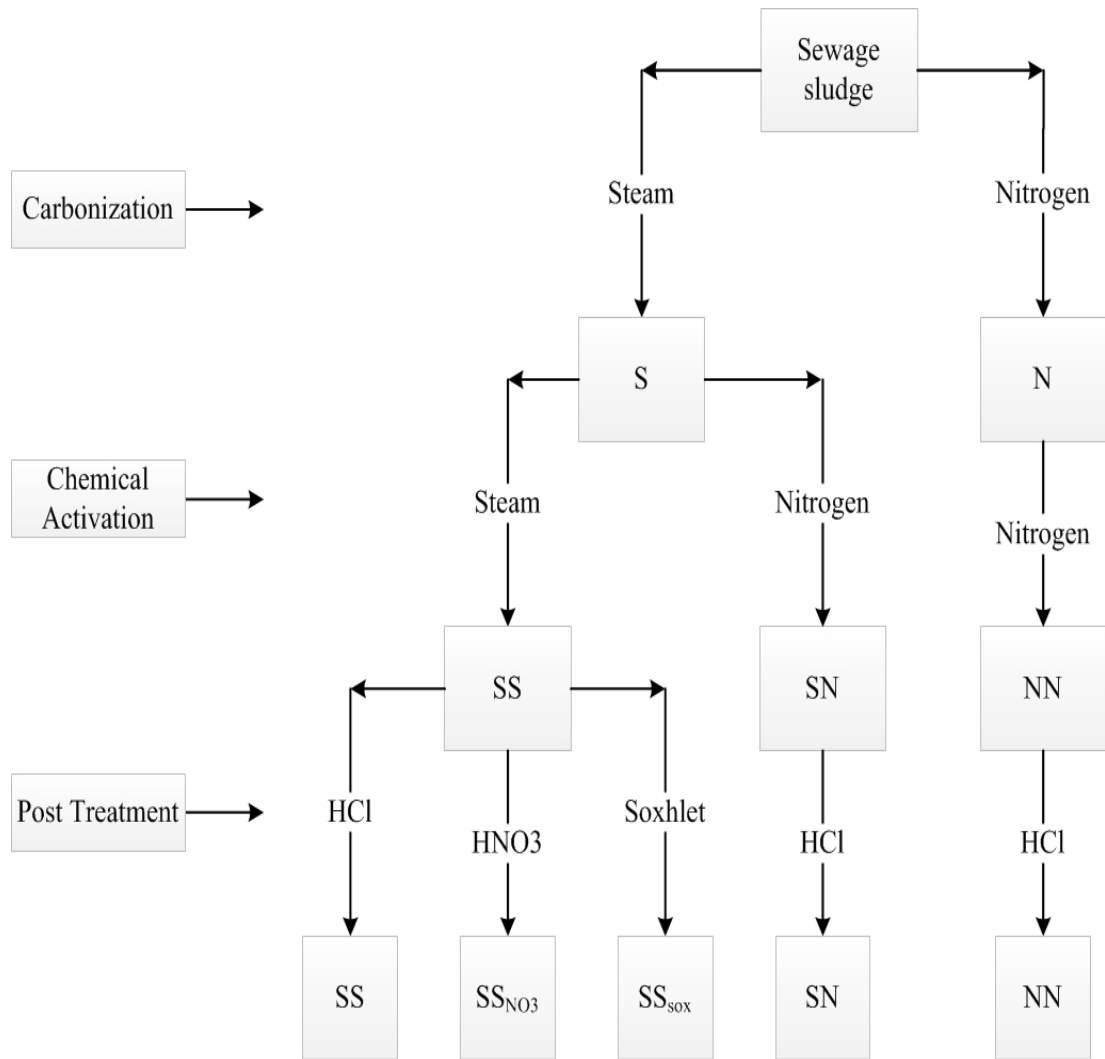


Figure 6: Flowchart for the production of activated carbons and carbonaceous materials by different methods

Table 10 summarizes the percent weight loss during carbonization and activation steps. For carbonization under steam environment a percent weight loss of 61.3 was observed. For the carbonization under nitrogen environment a percent loss of 63.1 was observed. So the weight loss for carbonization step is almost the same for both methods. For the activation under steam environment of the S-carbonized material a weight loss of 58.5 percent was noted where a weight loss of 51.2 percent was observed for activation under nitrogen environment. For N-carbonized material a weight loss of 50.5 percent is observed during activation under nitrogen environment. Total weight loss during all three methods is almost the same i.e. 83.9, 81.1 and 81.7 respectively.



Table 10: Percent mass loss during activation

Carbonization Environment	Percent Mass Loss during Carbonization	Activation Environment	Percent Mass Loss during Activation	Percent Total Mass Loss
Steam	61.3	Steam	58.5	83.9
Steam	61.3	Nitrogen	51.2	81.1
Nitrogen	63.1	Nitrogen	50.5	81.7

Table 11 indicates which analyses were performed on each activated carbon and carbonaceous material.

Table 11: Analyses performed on the activated carbons and carbonaceous materials

Analysis IDs	BET Surface Area	N <sub>2</sub> Adsorption	DFT	TGA	SEM	Elemental Analysis	Boehm and pH	Pb Sorption
S	✓			✓	✓	✓	✓	
SS	✓	✓	✓	✓	✓	✓	✓	✓
SS <sub>NO3</sub>					✓		✓	
SS <sub>SOX</sub>					✓		✓	
N	✓			✓	✓	✓	✓	
NN	✓	✓	✓	✓	✓	✓	✓	✓
SN	✓	✓	✓	✓	✓	✓	✓	
CAC	✓	✓	✓	✓	✓	✓	✓	✓

### 7.1. Nitrogen Adsorption Isotherms

BET surface areas, pore volumes and pore diameters are given in Table 12. BET surface area is illustrated in Figure 7. For S and N carbons no appreciable surface area was generated as shown in table 12. SS, NN and SN samples have BET surface area between 800 and 1000 m<sup>2</sup>/g and micropore areas between 500 to 700 m<sup>2</sup>/g. Total pore volume of the three activated carbons ranges from 0.52 to 0.62 cm<sup>3</sup>/g

and the average pore diameters were similar, at 24 to 25 Å. This indicates that the type of the pores generated depends on the chemical activation employed alone that is KOH in this case and does not depend on environment of the activation step i.e. steam or nitrogen. Looking at the total surface areas the chemical activation under nitrogen environment has created only slightly more pores than the activation under steam environment and the difference is in the micropore area. Commercial activated carbon Norit has a BET surface area of 1078 m<sup>2</sup>/g and a low micropore area 436 m<sup>2</sup>/g as compared to SS, NN and SN activated carbons. Total pore volume 0.987 cm<sup>3</sup>/g and average pore diameter 36.9 Å are much greater for CAC as compared to SS, NN and SN activated carbons. The fraction of micropore area for sludge based sorbents i.e. SS, NN and SN is approximately 0.65 to 0.7 whereas the fraction of micropore area for commercial activated carbon CAC is 0.404.

Table 12: Porosity characterization of activated carbons obtained from the KOH activation

Sample ID	BET Surface Area (m <sup>2</sup> /g)	Micropore Area (<20) (m <sup>2</sup> /g)	Mesopore Area (>20 Å) (m <sup>2</sup> /g)	Total Pore Volume (cm <sup>3</sup> /g)	Smic/SBET	Average Pore Diameter by BET (Å)
S	1.71*	1.84*	-	0.0053*	-	117.5*
SS	838	558	280	0.524	0.666	24.6
N	3.96*	not measurable	-	0.004*	-	43.7*
NN	1019	702	317	0.618	0.689	23.8
SN	887	572	315	0.565	0.645	25.1
CAC	1078	436	642	0.987	0.404	36.9

**Note** \*Samples S and N tested so low in surface area that the carbon method utilized is not appropriate to accurately characterize them.

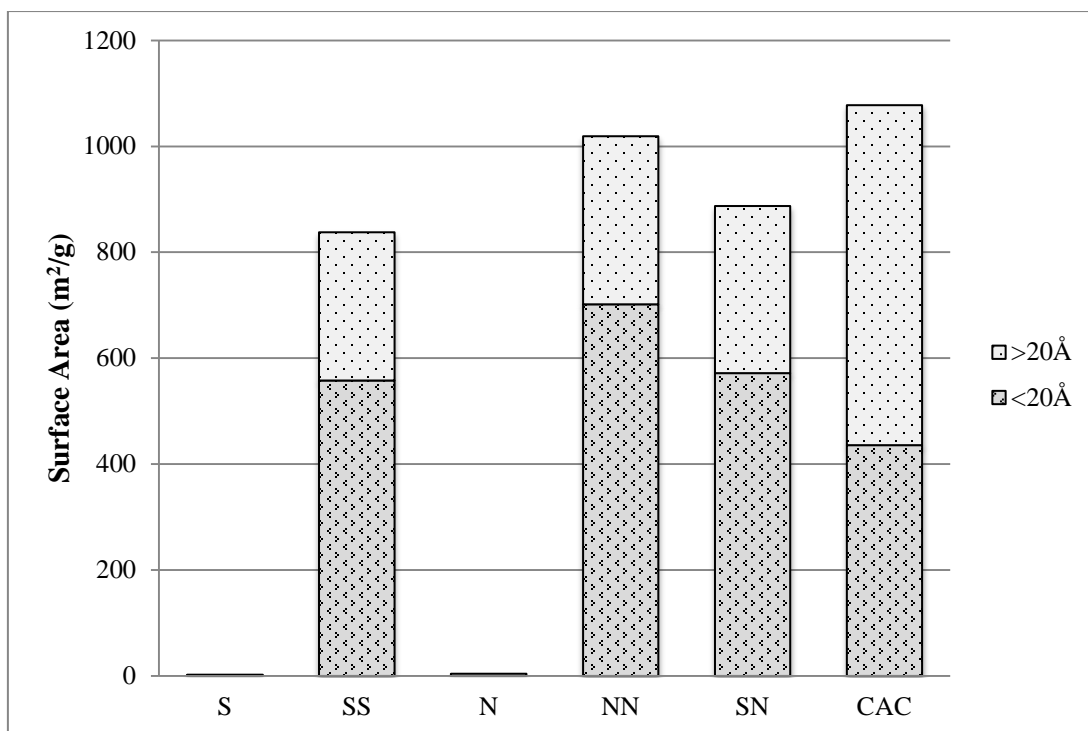


Figure 7: BET surface area distribution

Fig 8 shows the nitrogen adsorption-desorption isotherms at a temperature of 77K for SS, NN, SN and CAC activated carbons. The isotherms for SS, NN and SN belong to type H4 of the IUPAC classification of adsorption-desorption hysteresis loops. There is a complete overlap for the isotherms at low relative pressure  $P/P^0$  and the hysteresis loop exists at higher relative pressure, which indicates the presence of slit shape pores. The initial part of the isotherms of SS, NN and SN shows a large uptake which indicates the presence of micropores and mesopores, it can also be seen from average pore diameter of 25.1 Å by BET. The initial uptake for NN is a lot more as compared to SS, SN and CAC which is due to the large micropore area for NN. The amount of nitrogen adsorbed at high relative pressure  $P/P^0$  increases for the commercial activated carbon that shows a wide distribution of pore sizes, mainly in mesopore area and this is also indicated by average pore diameter by BET i.e. 36.9 Å. The isotherm for the commercial activated carbon shows a hysteresis loop that is intermediate between type H3 and H4, and for which the type of pores is slit shape.

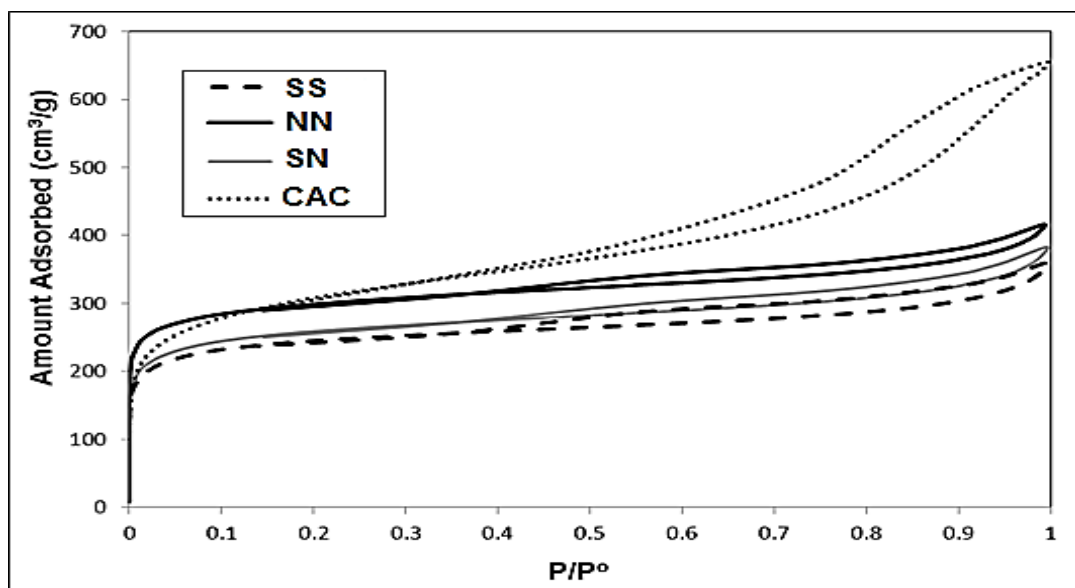


Figure 8: Adsorption/desorption isotherms of N<sub>2</sub> at 77 K for KOH activated carbons

Table 13 and Figure 9 present the porosity distribution data by original density functional theory (DFT) for SS, NN, SN and CAC activated carbons. Pore volume for micropore region i.e.  $V_{<10 \text{ Å}}$  is from 0.18 to 0.25 cm<sup>3</sup>/g for SS, NN and SN sorbents where the micropore volume for  $V_{<10 \text{ Å}}$  is much less for commercial activated carbon (CAC) i.e. 0.125 cm<sup>3</sup>/g. For all sorbents SS, NN, SN and CAC micropore volume for  $V_{<20 \text{ Å}}$  is approximately 0.3 cm<sup>3</sup>/g. Commercial activated carbon CAC exhibits a large total volume of 0.918 cm<sup>3</sup>/g as compared to the total volume of SS, NN and SN activated carbons i.e. approximately 0.5 cm<sup>3</sup>/g. Therefore sludge based sorbents SS, NN and SN are diametrically opposite to the commercial activated carbon CAC, having larger  $V_{<10 \text{ Å}}$  of approximately 0.2 cm<sup>3</sup>/g and smaller total volumes i.e. 0.5 cm<sup>3</sup>/g as compared to 0.918 cm<sup>3</sup>/g for CAC.

Table 13: Porosity characterization of adsorbents obtained from KOH activation of different activated carbons by N<sub>2</sub> adsorption at 77K

Sample ID	Specific Pore Volume (cm <sup>3</sup> /g)			V <sub>mic</sub> /V <sub>T</sub>
	V <sub>&lt;10Å</sub>	V <sub>&lt;20Å</sub>	V <sub>T</sub>	
SS	0.183	0.286	0.482	0.593
NN	0.250	0.344	0.473	0.728
SN	0.193	0.299	0.513	0.582
CAC	0.125	0.303	0.918	0.330

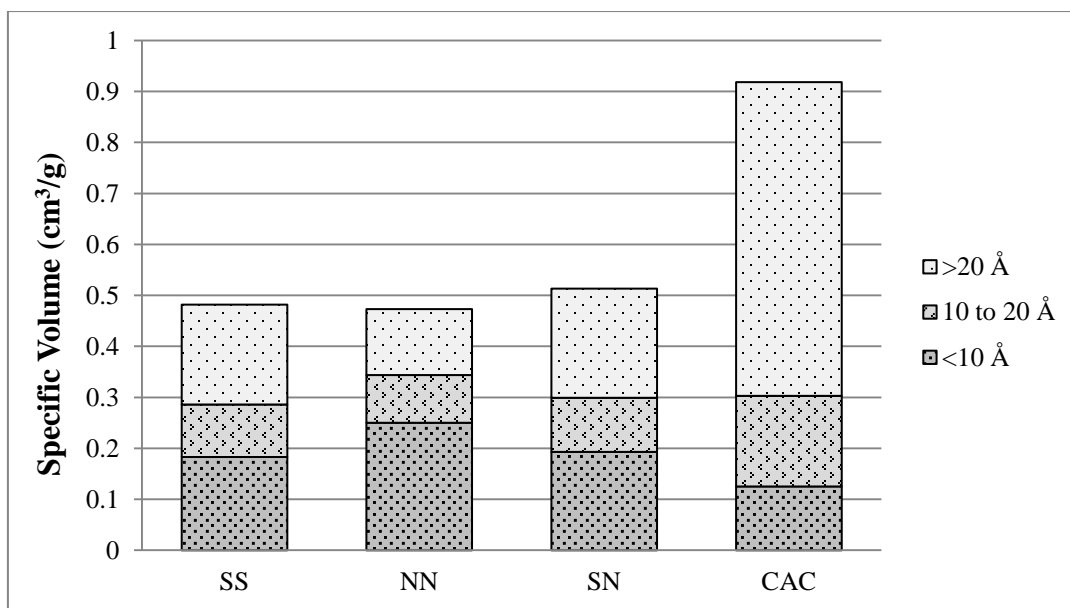


Figure 9: Specific volume pore distribution

Figure 10 presents the plot for the porosity distribution of activated carbons by original density functional theory (DFT). For sludge based sorbents (SS, NN and SN) the peaks for micropore and mesopore regions appear at 9 Å and 19 Å respectively with the highest micropore volume for NN activated carbon. SS, NN and SN activated carbons appear to have limited macropore volume as compared to commercial activated carbon CAC which shows a large fraction of volume in macropore region.

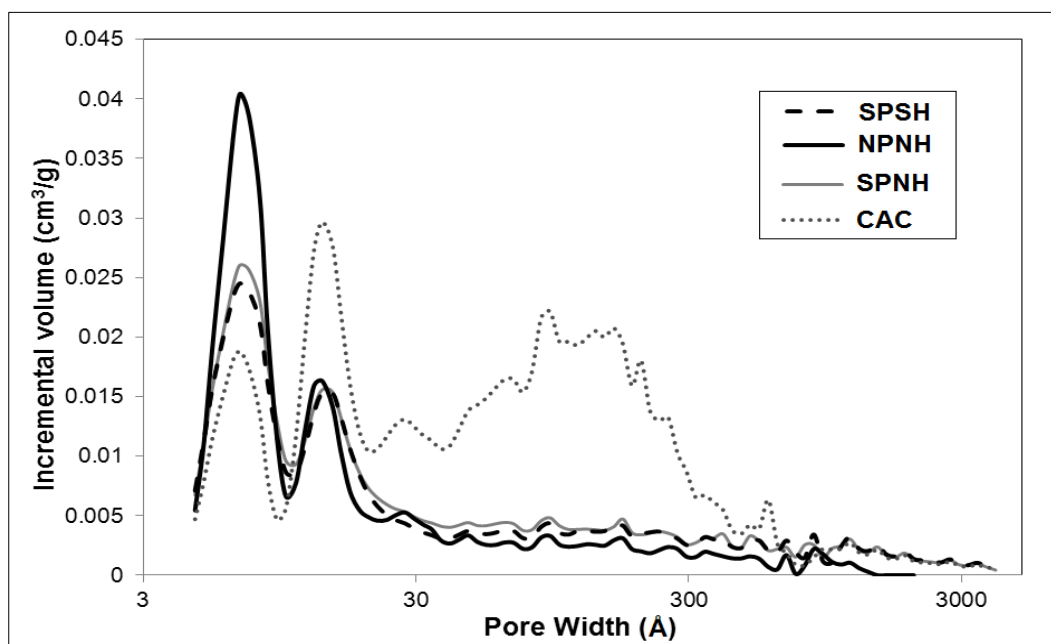


Figure 10: Porosity distribution of KOH activated carbons by original density functional theory (DFT)

## 7.2. Thermal Gravimetric Analysis

Thermal gravimetric analysis of different samples of activated carbon is given in table 14. The carbonized samples S and N revealed approximately 50% ash contents, this means that after carbonization the carbonaceous material is 50% carbon and 50% ash. Activated carbons SS, NN and SN contain less ash contents which show significant removal of inorganics during chemical activation. The sludge based sorbent activated under steam environment SS has the least ash at half as much as NN and SN activated under nitrogen environment. The commercial activated carbon CAC exhibited very small ash contents of 1.68%.

Table 14: Thermal gravimetric analysis of KOH activated carbons

<b>Experimental Carbon Sample ID</b>	<b>Weight Loss % to 150°C</b>	<b>Weight Loss % 150°C to 654°C</b>	<b>Weight Loss % 654°C to 800°C</b>	<b>Residue at 800°C</b>	<b>Appearance of Residue</b>
S	2.51	13.8	30.1	53.6	Orange powder
SS	6.26	7.32	71.8	14.6	Orange powder
N	3.48	15.3	33.7	47.5	Orange powder
NN	6.31	15.7	49	29	Red Orange powder
SN	7.52	9.81	49.4	33.2	Red Orange powder
CAC	4.14	16.4	77.8	1.68	A few hard black bits

## 7.3. Elemental Analysis

Table 15 shows the elemental composition of 5 samples of sludge based sorbents i.e. S, SS, N, NN, SN and commercial activated carbon CAC. A full area EDAX scan was carried out resulting in the elemental analysis of particular area chosen; selecting a different spot may result in a slight difference in composition; still some important conclusions can be drawn from the analysis. Only the two carbonized samples S and N revealed a wide distribution of elements. They have carbon, oxygen and calcium in major proportions and other elements (sodium, magnesium, aluminum, silicon, phosphorous, sulfur, molybdenum, potassium and iron) in small amounts ranging from 1 to 9 %. Composition of the activated samples i.e. SS, NN and SN

showed that the activation process has eliminated much of the elements that were observed in the carbonized samples. Activation under steam environment has significantly increased the percentage of carbon to 78% in SS while the activation under nitrogen environment produced a carbon content of approximately 52% as shown under NN and SN. The percentage of carbon in NN and SN did not increase because the amount silicon, molybdenum and potassium increased during activation step. Interestingly, SS did not contain potassium, although KOH was used as the pre-activation chemical treatment and potassium is observed in SN and SS. Commercial activated carbon CAC exhibited a high percentage of carbon 96% and small amounts of oxygen and sulfur.

Table 15: Elemental analysis (wt. %) of KOH activated carbons

Element	Sample ID					
	S	SS	N	NN	SN	CAC
C	33.74	78.03	53.02	51.69	52.57	96.08
O	11.75	6.51	11.03	12.27	14.05	0.21
Na	1.02					
Mg	2.85		2.2			
Al	2.44		1.25		1.84	
Si	7.6	9.08	4.57	17.46	14.08	
P	8.96		5.78			3.71
S	2.7	6.38				
Mo			2.92	3.32	11.91	
K	1.51			4.57	5.56	
Ca	19.97		13.16			
Fe	7.45		6.08	10.68		

The EDAX analysis was also carried out on 6 to 8 localized spots for all sludge based sorbents. The results are presented in table 16 and 17 for SS and NN activated carbons only as the results for other samples are similar. The EDAX results for the localized spot analysis may be compared with the EDAX full area scan results given in table 15. The average percent amounts of elements for localized spot analysis is almost same as given in table 15, although results for each spot may differ significantly. Figure 11 shows the SEM micrographs of carbonized samples. Figure 12 shows the SEM micrographs of the sludge based activated carbons and the

commercial activated carbon. It can be seen clearly that structure of the carbonized samples S and N is similar and structure for the activated carbons SS, NN, SN, SS<sub>NO3</sub> and SS<sub>sox</sub> is also similar.

Table 16: Localized spot analysis for SS activated carbon

Element	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Average
C K	57.1	57.4	68.51	91.92	82.4	76.13	72.24
O K	7.7	11.17	7.82		13.12	6.84	7.78
Si K	16.58	14.24	12.86	4.14	2.43	8.47	9.79
Mo K		8.92					1.49
S K	7.04		3.99	3.94	2.04	8.56	4.26
Fe K	11.58	8.26	6.83				4.45

Table 17: Localized spot analysis for NN activated carbon

Element	Spot 1	Spot 2	Spot 3	Spot 4	Spot 5	Spot 6	Average
C K	87.66	77.79	55.64	42.18	20.68	45.79	54.96
O K	-	5.18	11.24	12.38	9.97	16.7	11.09
Si K	-	11.63	16.4	20.09	43.69	34.28	25.22
Mo K	9.51	-	-	3.86	-	-	6.69
Fe K	-	-	13.29	16.56	17.78	-	15.88
K K	2.83	5.4	3.43	4.93	7.88	3.23	4.62

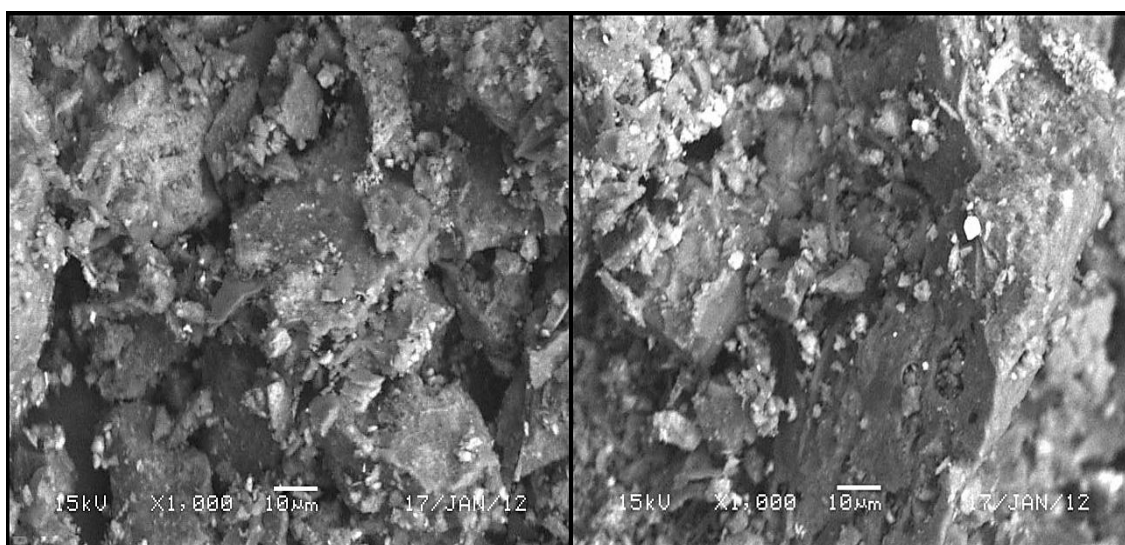


Figure 11: SEM Micrograph for carbonized samples (a) S and (b) N



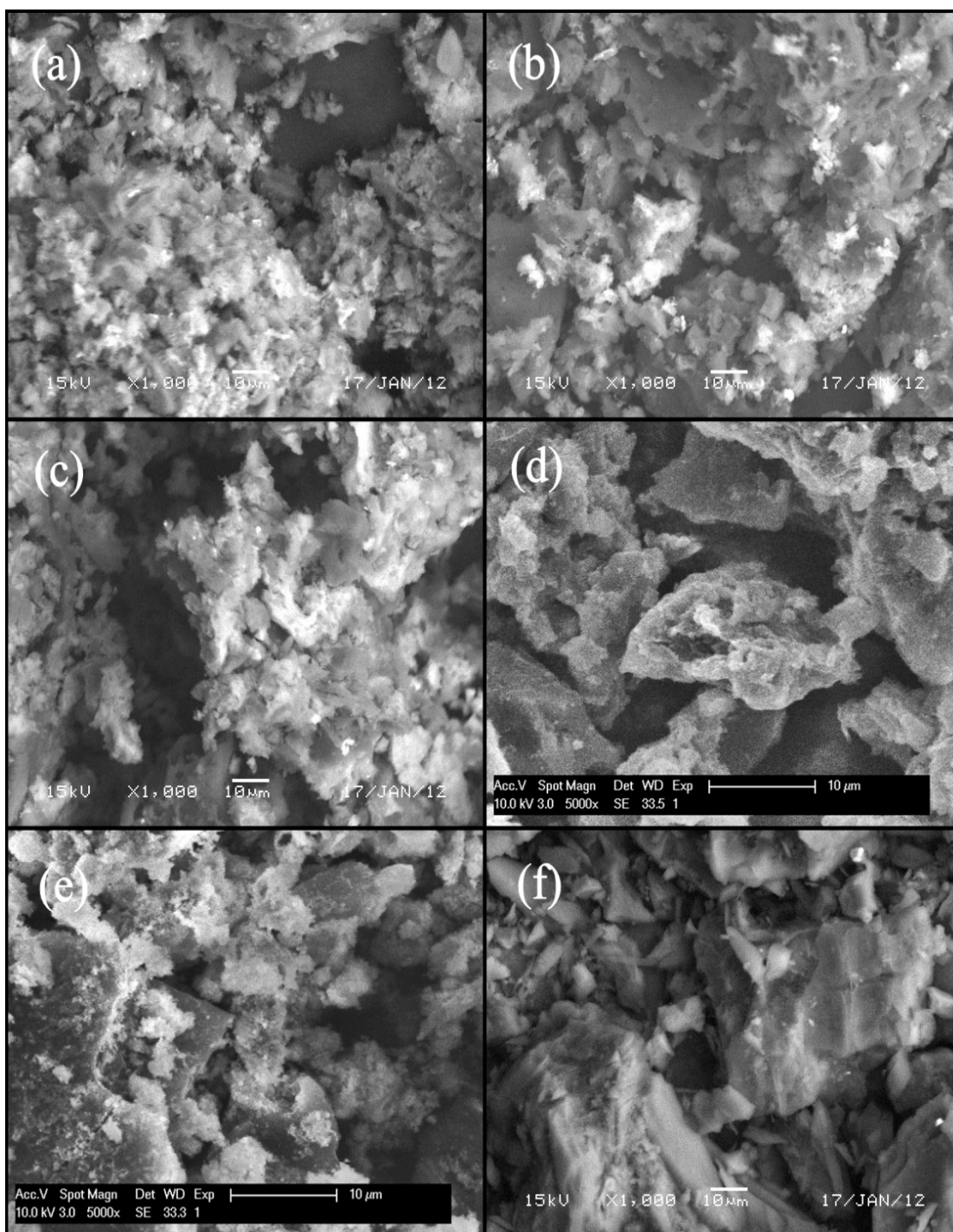


Figure 12: KOH activated carbons (a) SS (b) NN (c) SN (d) SS<sub>NO3</sub> (e) SS<sub>sox</sub> and commercial activated carbon (f) CAC

Figure 13 and 14 shows the micrographs of SS and NN activated carbons before and after the adsorption experiments for the 400 mg/L concentration of lead nitrate solution. It can be seen clearly that the after the adsorption experiment most of the surface of activated carbon is covered.

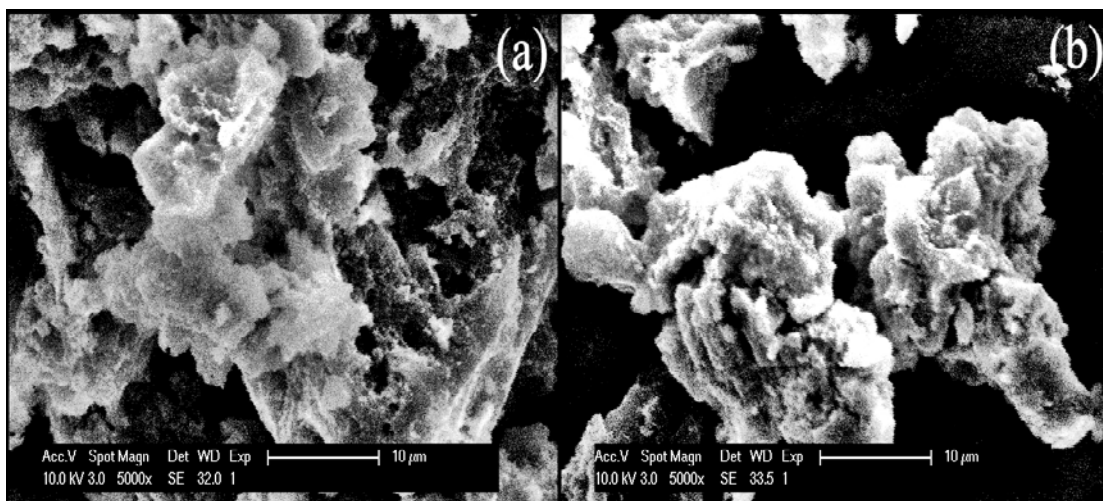


Figure 13: (a) SS activated carbon before adsorption (b) SS activated carbon after adsorption experiment with 400 md/L lead nitrate

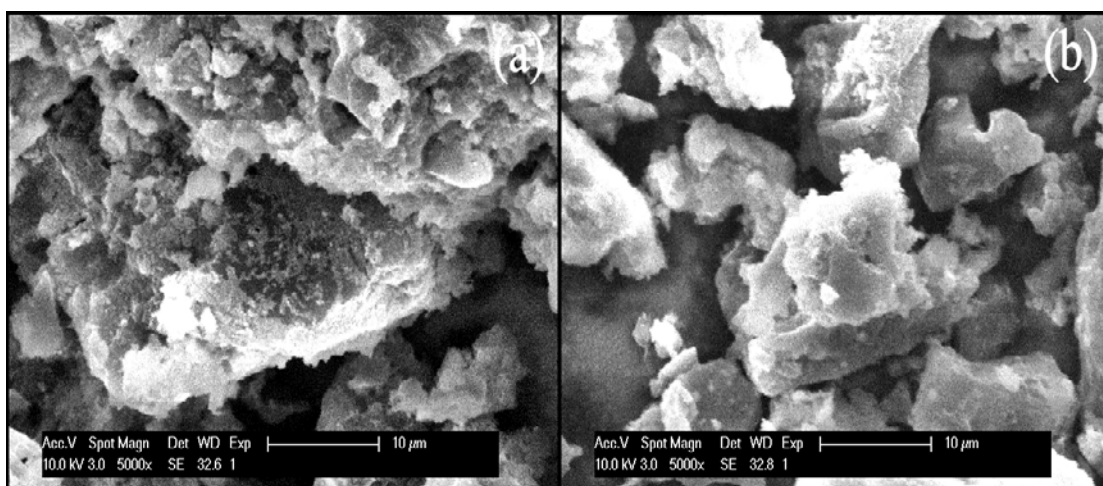


Figure 14: (a) NN activated carbon before adsorption (b) NN activated carbon after adsorption experiment with 400 md/L lead nitrate

## 7.6. BOEHM Titration and pH

The amount of acidic sites is calculated from the amounts of NaOH reacted with the carbon surface while the number of surface basic sites was calculated from the amount of hydrochloric acid consumed. The amounts of the acidic and basic functional groups as well as the pH values for various activated carbons are presented in table 18. Analysis of the data indicates that the two carbonized samples S and N are basic in nature showing high amounts of basic functional groups 4.40 and 4.12 mmol/g confirmed by the pH values 10.41 and 10.06 respectively. This shows that the carbonaceous material produced is similar from the two methods i.e. under nitrogen environment and the steam. It can be seen that there is a large change in the surface

chemistry of activated carbons after chemical activation and post-activation chemical treatment. The three activated carbons treated with HCl in post treatment SS, NN and SN show large amounts of acidic functional groups 3.13, 3.67 and 4.19 mmole/g respectively and relatively small amounts of the basic functional groups 1.146, 0.947 and 1.952 respectively. SS shows highly acidic nature as shown by its pH value 2.82; NN is less acidic at a pH of 5.60 and SN shows a neutral behavior at a pH of 7.06. Among the steam activated carbons SS and SN show high amounts of acidic functional groups 3.13 and 3.43 mmol/g and acidic pH values 2.82 and 3.22 respectively; SS<sub>sox</sub> activated carbon rinsed in soxhlet shows a basic behavior with high amount of basic functional groups 5.532 mmol/g and a basic pH 8.64. This shows that post treatment with an acid has shifted the behavior of activated carbon from basic to acidic as shown by SS<sub>sox</sub>. Commercial activated carbon CAC shows highly acidic behavior with 2.255 mmol/g acidic functional groups and a pH of 2.73.

Table 18: Amount of acid and basic groups and pH for activated carbons and carbonaceous materials

Sample ID	Acidic Groups (mmol/g)	Basic Groups (mmol/g)	Total (mmol/g)	pH
S	0.635	3.768	4.403	10.41
SS	3.13	1.146	4.276	2.82
SS <sub>NO3</sub>	3.429	0.897	4.326	3.22
SS <sub>sox</sub>	0.678	5.532	6.209	8.64
N	0.583	4.119	4.702	10.06
NN	3.668	0.947	4.615	5.6
SN	4.192	1.952	6.144	7.06
CAC	2.255	0.05	2.305	2.73

### 7.7. Lead (Pb) adsorption isotherms

The experimental results corresponding to the adsorption of lead (Pb) for the sludge based activated carbons NN and SS and commercial activated carbon CAC are given in Figure 15 and 16. Equilibrium time was estimated to be 48hr for the sludge based activated carbons. Clearly the two sludge based activated carbons show different behavior for the adsorption of lead. The adsorption capacity of NN activated carbon is higher as compared to SS activated carbon. The higher adsorption capacity of NN can

be attributed to its higher BET surface area and higher micropore volume as compared to SS. Adsorption results for the two runs for both activated carbons NN and SS show an excellent reproducibility. Commercial activated carbon CAC and sludge based activated carbon SS are similar as they show approximately same adsorption capacity.

Langmuir, Freundlich, Toth and Langmuir-Freundlich adsorption isotherms were employed to estimate the maximum adsorption capacity of the two sludge based activated carbons NN and SS and commercial activated carbon CAC. Fitting of the four sorption isotherms is shown in Figure 17 through 21 and the parameters corresponding to the fitting of the adsorption results to the adsorption isotherms are reported in table 18. Adsorption capacity estimated by Langmuir sorption isotherm for the activated carbons NN, SS and CAC is 26.9, 15 and 11.2 mg/g respectively is much lower than those estimated by Toth and Langmuir-Freundlich sorption isotherms for the activated carbons NN, SS and CAC i.e. 73.34, 51.6, 42.5 mg/g and 71.2, 49.2, 45.6 mg/g respectively. Parameters for the Freundlich sorption isotherm  $n$  and  $K_f$  for NN, SS and CAC activated carbons are 2.77, 3.32, 2.1 and 3.5, 2.83, 1.25 respectively which show favorable sorption. Also fitting of the parameters for the Langmuir is poor as compared to the Freundlich, Toth and Langmuir-Freundlich sorption isotherms. So the results for sorption capacity of NN, SS and CAC activated carbons for lead estimated by Langmuir sorption isotherm can be rejected.

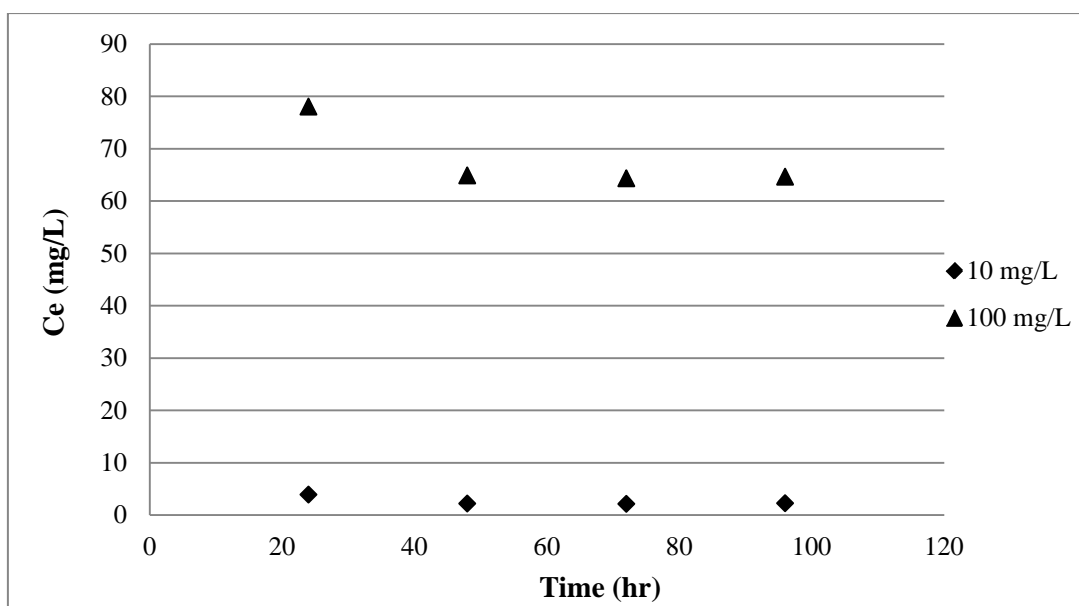


Figure 15: Equilibrium time for KOH activated carbons

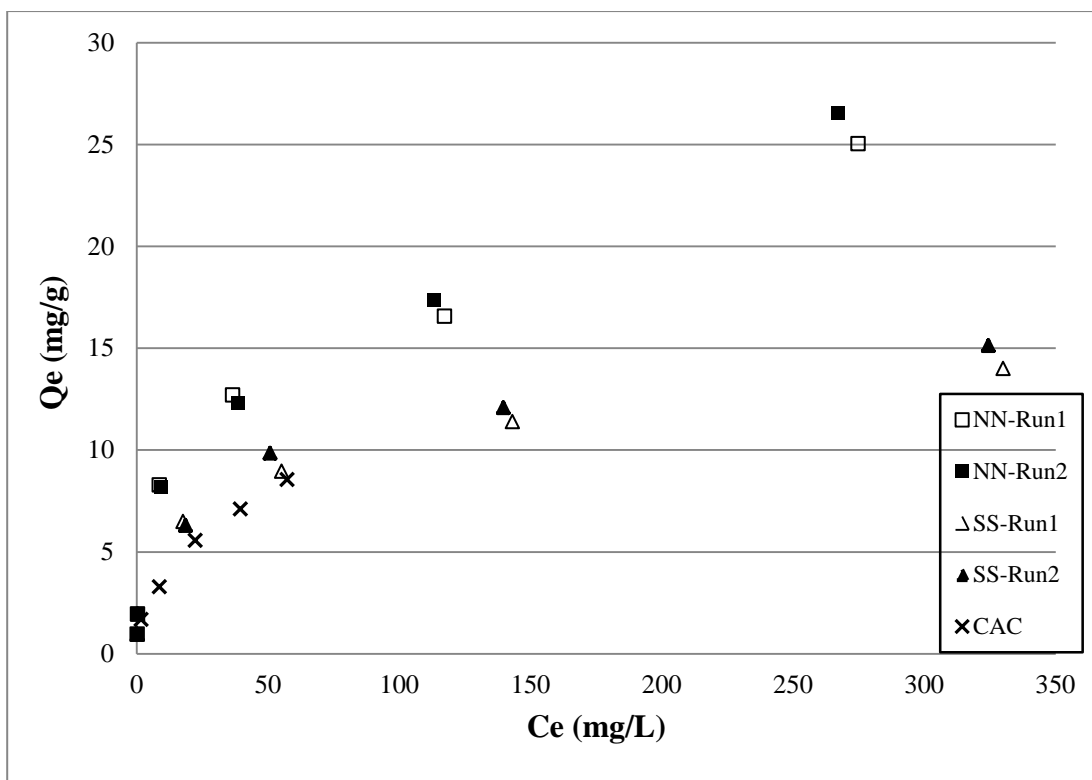


Figure 16: Adsorption results for NN and SS activated carbons

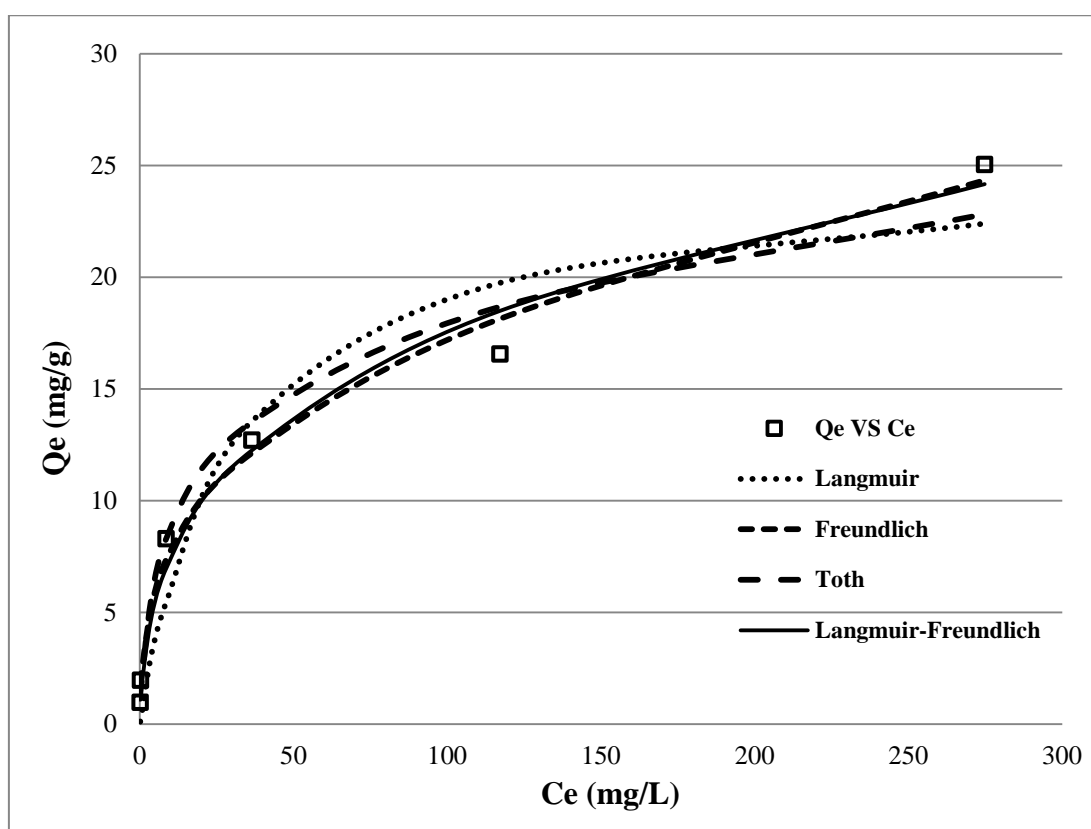


Figure 17: Fitting of adsorption isotherms for NN Run1

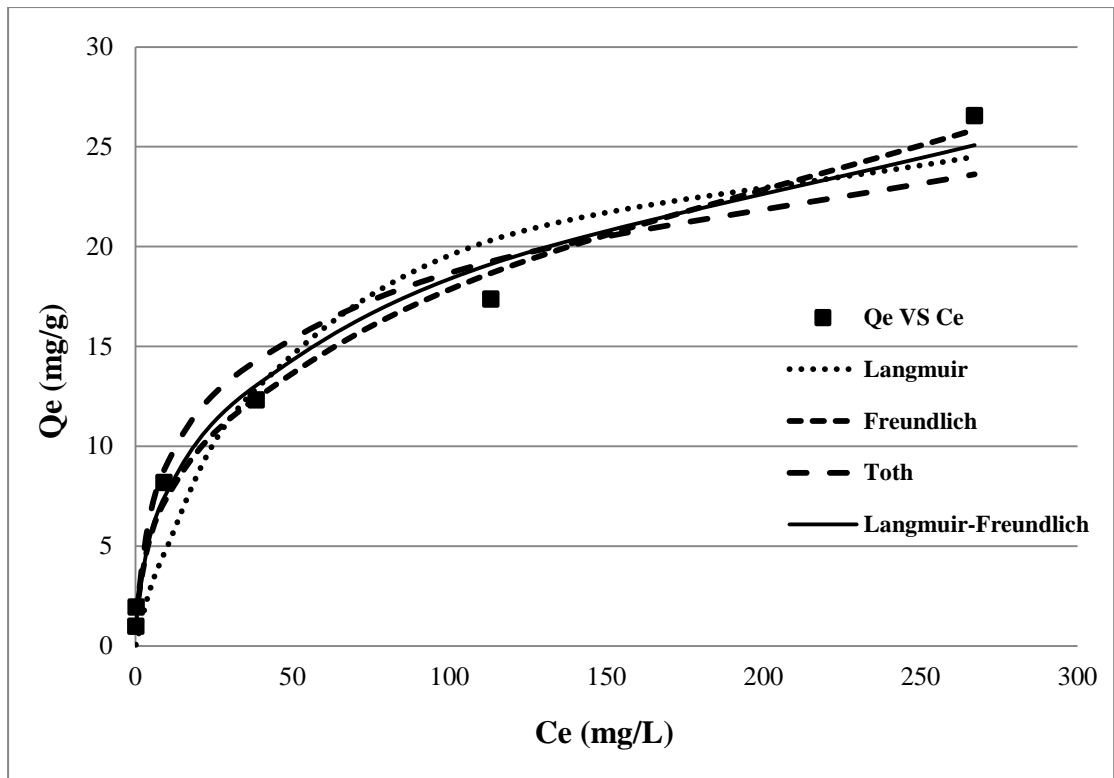


Figure 18: Fitting of adsorption isotherm for NN Run 2

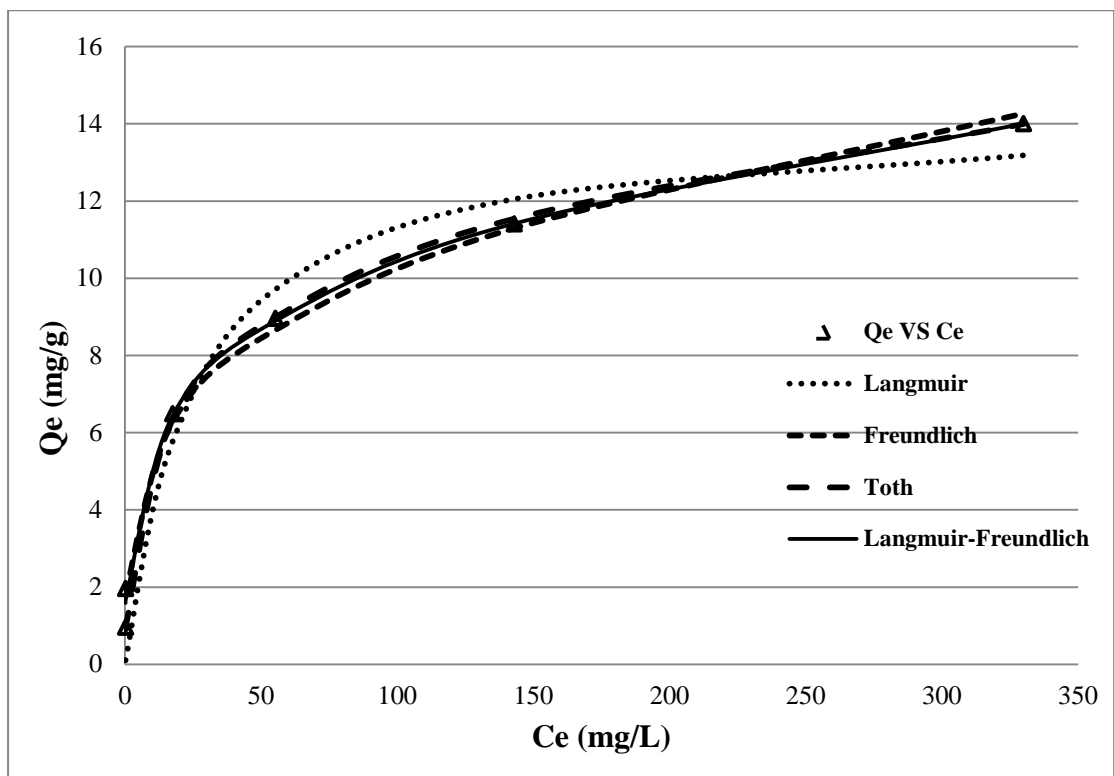


Figure 19: Fitting of adsorption isotherms for SS Run1

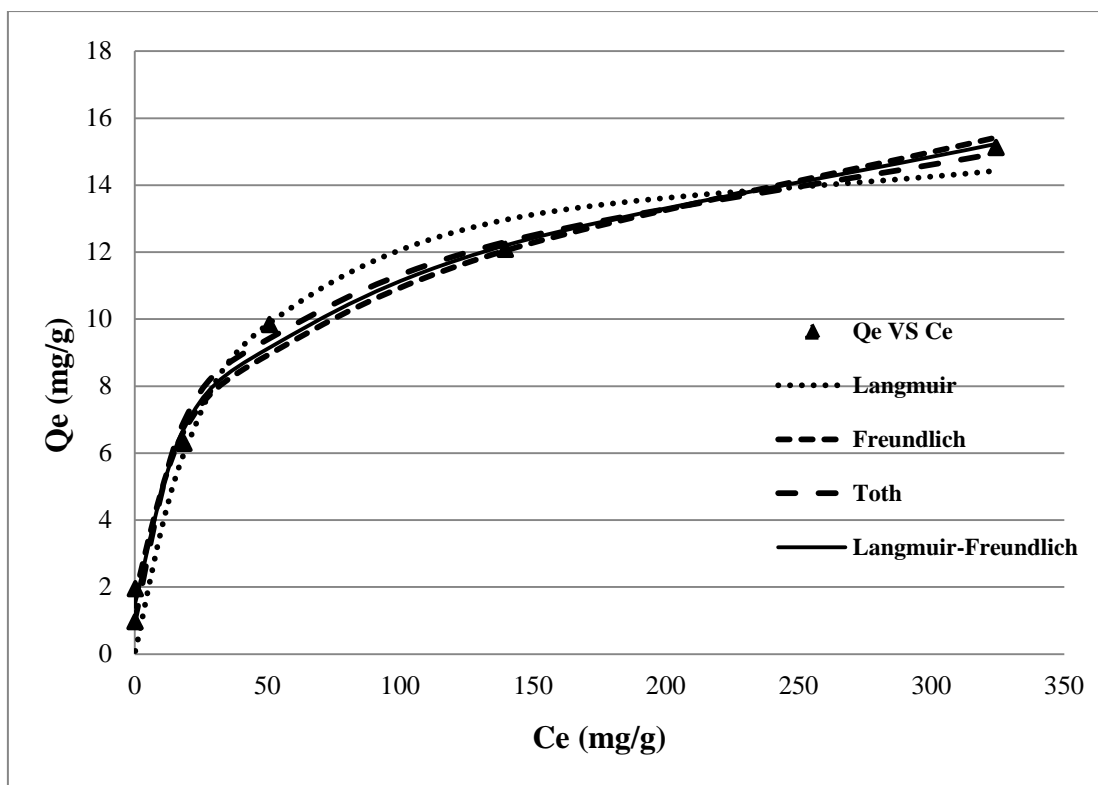


Figure 20: Fitting of adsorption isotherm for SS Run2

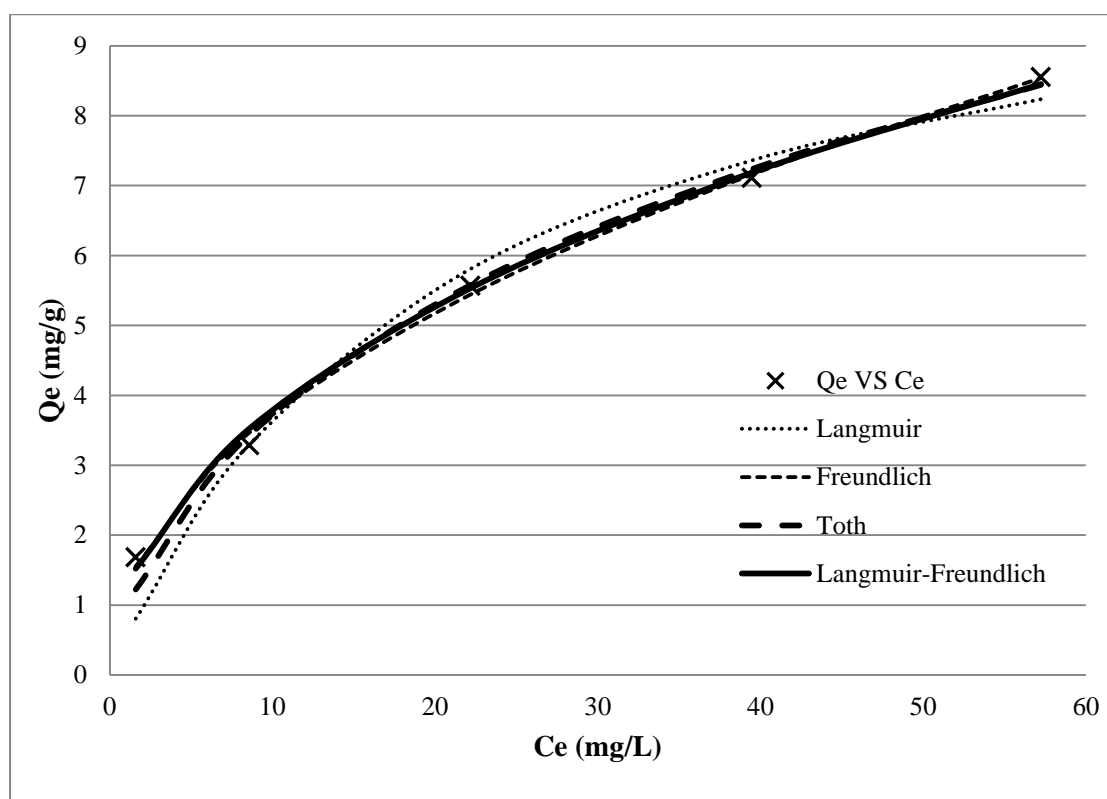


Figure 21: Fitting of adsorption isotherms for commercial activated carbon CAC

Table 19: Parameters corresponding to the fitting of the adsorption results to the adsorption isotherms

Sorbent		NN-B1	NN-B2	SS-B1	SS-B2	CAC
Sorbate		Pb				
Final pH		3.5-4.5	3.5-4.5	3.5-4.5	3.5-4.5	3.5-4.5
Langmuir	$Q_{\max}$ (mg/g)	24.89	28.88	14.21	15.78	11.196
	$K_a$ (L/mg)	0.033	0.021	0.039	0.033	0.049
	$R^2$	0.929	0.937	0.953	0.966	0.967
Freundlich	$n$	2.901	2.640	3.580	3.410	2.105
	$K_f$	3.513	3.120	2.830	2.830	1.248
	$R^2$	0.988	0.993	0.993	0.990	0.998
Toth	$K_t$ (mg/g)	70.64	76.05	49.15	54.07	45.611
	$a_t$	0.950	0.940	0.850	0.830	0.027
	$t$	0.218	0.214	0.194	0.190	1.899
	$R^2$	0.975	0.965	0.993	0.991	0.997
Langmuir-Freundlich	$Q_{\max}$ (mg/g)	70.03	72.33	47.01	51.37	42.525
	$K$	0.042	0.042	0.061	0.053	2.400
	$n$	2.220	2.203	2.990	2.788	0.316
	$R^2$	0.984	0.986	0.996	0.994	0.992

## 8. Conclusions

In this study, activated carbon is produced using a conventional method described in literature [14]. A new method was developed to convert sewage sludge into activated carbon in steam environment without using an external flowing stream. Activated carbons were analyzed by sorption of nitrogen, Boehm titrations, pH measurement, thermal analysis (DTA and DTG analysis), ash content, scanning electron microscope (SEM)/energy-dispersive X-ray spectroscopy (EDS), elemental analysis and adsorption of lead isotherms. Results for the sewage sludge based activated carbons were compared with commercial activated carbon i.e. Norit.

- During the production of activated carbons from sewage sludge, a mass loss of 81 to 83% was observed.



- The maximum surface area of 1019 m<sup>2</sup>/g was achieved for activation under nitrogen environment (NN) in comparison to the 1078 m<sup>2</sup>/g surface area of commercial activated carbon CAC.
- Activated carbon, SS, produced in a steam environment under static condition of no external flowing stream achieved a surface area of 838 m<sup>2</sup>/g
- Nitrogen adsorption / desorption isotherms showed the presence of micro and meso pores with an average pore size 25 Å for sludge based adsorbents, whereas for commercial activated carbon CAC a wider distribution of pore sizes was observed with an average pore size of 37 Å.
- Carbonized samples showed high ash contents of 50 %. Activation reduced the ash content considerably from 14 to 30 %. Commercial activated carbon showed only 1.7 % ash contents.
- Elemental analysis revealed high proportion of inorganic contents in sludge based activated contents. Potassium was not observed in SS, although KOH was used for the chemical activation, where NN and SN activated in nitrogen environment possess about 5 percent potassium by weight. Commercial activated carbon possesses no metallic contents.
- Acid post treatment Sludge based activated carbons decreased the amount of surface basic groups and increased the amount of surface acidic groups. SS, SS<sub>NO3</sub>, NN exhibit acidic pH, SN is neutral and activated carbon rinsed in soxhlet SS<sub>sox</sub> is basic with a pH of 8.6; All sludge based activated carbons possess high amount of surface functional groups 4 to 6 mmol/g. Commercial activated carbon CAC is acidic, pH 2.7 and total surface functional groups 2.3 mmol/g.
- Adsorption studies were measured for lead nitrate. Sludge based activated carbon produced in nitrogen environment NN showed the highest adsorption capacity of approximately 75 mg/g. Adsorption capacity for sludge based activated carbon produced without an external flowing inert stream SS and commercial activated carbon possess similar adsorption capacity i.e. 50 and 46 respectively.

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## **Vita**

Saeed ur Rehman was born on April 18, 1987, in Pindi Gheb, Pakistan. He was educated in local public schools and graduated from Government High School as best student in 2003. He received scholarship from Government of District Attock for being one of the best students in district. He joined Pre-Engineering program at Government Degree College Pindi Gheb and graduated in 2005. He received a certificate of Fundamentals of Science in Pre-Engineering. He selected chemical engineering as his professional career and joined University of Engineering and Technology (UET) Lahore for the undergraduate studies. He graduated from UET Lahore in 2009 and his degree was Bachelor of Science in Chemical Engineering.

Mr. Saeed shifted to United Arab Emirates in 2010 and worked in William Hare LLC as Co-ordination Engineer for six months. In September 2010 he started his graduate level studies in chemical engineering at American University of Sharjah (AUS). He got the award of Graduate Assistant at AUS and graduated in 2012. His degree was Master of Science in Chemical Engineering.