ADSORPTION OF METALS IN FLU-GAS DESULFURIZATION WASTEWATER

BY IRON-IMPERGNATED ACTIVATED CARBON

By

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Abstract

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The combustion of coal releases flue gases into the atmosphere, which have high concentrations of sulfur oxides ($SO_x$). $SO_x$ emissions cause serious impacts on the environment and human health. Flue gas desulfurization (FGD) technologies are installed in almost all the coal fired power plants. Wet FGD technology is used more extensively to treat the flue gas, as it is cost efficient and also the reduction efficiencies are very high. Despite the treatment process available for treating FGD wastewater, achieving the effluent limitations by using these processes is very tedious and expensive. In this study, granular activated carbon (GAC), GAC impregnated with iron (GAC/FeO$_x$) and GAC impregnated with zerovalent iron (GAC/ZVI) were used to treat the FGD wastewater. The application of the modified GAC materials for treatment of FGD wastewater is a new approach. Adsorption batch experiments were conducted and adsorption kinetics for various metal components was studied. The results showed reduction in the concentration levels of metal compounds such as mercury, lead, copper, arsenic, and chromium. This research paves way for further understanding of the FGD wastewater and its treatment process.
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Chapter 1

Introduction

1.1 Summary

Sulfur dioxide emissions from the coal fired power plants has been main concern to environmentalists for the past few years. Coal has been the main source for the production of electricity. The emissions from the combustion of coal contain very high concentration of sulfur dioxide and nitrogen oxides. Reduction of sulfur dioxide concentration in the emission gas, so-called flue gas, is very important as it has very serious environmental and health impacts. Acid rain is the main environmental concern. It also causes damage to the monuments and crops and also acidifies the lakes and rivers [1][2][5]. Flue gas desulfurization (FGD) technologies are used to reduce sulfur dioxide concentration in the emissions from the coal fired power plants. These FGD systems are classified as wet, dry and semi dry. These FGD technologies have been proven to be efficient in reducing the sulfur emissions [18][22]. Over the years the FGD technologies have further evolved in design, application and utilization. Among many FGD technologies available, wet lime process is actively used due to its cost effective nature and the efficient reduction sulfur dioxide from flue gas [7][8][16].

The wastewater produced from the FGD systems is our main concern. The FGD wastewater contains very high total suspended solids (TSS), heavy metals, and trace elements such as mercury [22]. Reducing heavy metals and trace elements from the FGD wastewater is a very tedious process. Concentration of these elements should match the guidelines set by the US Environmental Protection Agency (EPA), which will become significantly tight soon enough for current technologies to be ineffective to meet the new upcoming guidelines. Presently few treatment systems are available for the wastewater produced from the FGD systems such as the physical-chemical treatment,
biological treatment and construction wet lands treatment. All these processes are effective only for certain target elements. The treatment is selected based on which element we need to reduce the most. They also require large amount of space. Due to the concerns related to space and also to more target elements rather than one single element, a better treatment process is needed. This thesis works on developing a more effective and economical treatment process for the FGD wastewater [15-25].

Activated carbon sorption process is proposed to achieve the objective of the research. The FGD wastewater is treated with activated carbon to adsorb the metals and trace elements. The process is further developed by impregnating granular activated carbon (GAC) with iron oxides (GAC/FeO\textsubscript{x}) or zerovalent iron (GAC/ZVI) for the effective treatment of FGD wastewater. Iron impregnated activated carbon has been reported to be more effective for adsorption of some metals such as arsenic than bare activated carbon.

The main objective of this research is to develop a treatment method for the removal of metals in FGD wastewater by using the modified GAC materials. The effectiveness of GAC, GAC/FeO\textsubscript{x}, and GAC/ZVI to remove heavy metals in FGD wastewater is investigated and their performance is compared to elucidate the impacts of the iron modification. This is a new approach towards treating FGD wastewater. FGD wastewater from a wet FGD system provided by Southern Company is tested. The GAC materials are prepared by following the method established by Choi et al., which is composed of incipient wetness iron impregnation into GAC, heat treatment at high temperature (GAC/FeO\textsubscript{x}), and borohydride reduction of FeO\textsubscript{x} (GAC/ZVI) [50]. Through adsorption
batch tests, adsorption kinetics of various metal components, including mercury, selenium, arsenic, lead, copper and chromium, are observed.

This thesis is organized with 4 chapters, as follows:

Chapter 1 provides the general information on the research including study justification and objective. First, it provides information on coal combustion, coal fired power plants and the flue gas emissions, the impacts of sulfur dioxide emissions, and the need for reduction of sulfur dioxide concentration in the emissions. It gives a review of various types of FGD systems available and methods for the treatment of FGD wastewater. It gives the information on the need for treatment of FGD wastewater and effluent limitations and regulations for potential pollutants.

Chapter 2 gives information on experiment, the water being used for the research and a brief introduction to the inductively coupled plasma-mass spectroscopy (ICP-MS). It also gives details regarding the development of method for the experiment and process for the preparation of GAC impregnated with iron and GAC impregnated with zero valent iron.

Chapter 3 has the results and discussion of the experiment. These results are then analyzed and studied to see any significant reduction in the concentrations of the regulated metals.

Chapter 4 provides the conclusions of the research. It addresses the improvements that has to be made for the experimental procedure to get suitable results and also throws light on the possible errors that may be occurred during the experiment.
1.2 Coal

1.2.1 Coal and its importance

Coal has been in use by man for centuries for various purposes. Today coal is majorly used for the production of electricity. United States, China, Australia and India have abundant coal reserves. In United States coal is the major source of energy for the production of electricity. Electricity is a necessity of human life that the usage has been increasing day by day. The consumption of coal to meet the ever increasing demand for electricity is also huge. Thus we have environmental concerns associated with every aspect of coal such as excavations for coal and processing of coal [1-4].

![Figure 1-1 coal fields over United States (source: USGS)](image)

Coal is formed when swamps and peat bogs (dead plant material) are buried deep into the earth’s crust due to formation of silt, sediments above them and also due to the tectonic movements that takes place in the earth’s crust. Due to the depths that they get buried into, the dead plant material is subjected to high temperatures and pressures [1-2]. Thus coal is formed due the changes which are both physical and chemical caused.
by the high temperatures and pressures. Coal is a called a fossil fuel because it contains carbon which combines with hydrogen naturally to form hydrocarbons. Since fossil fuels are naturally occurring sources of energy and they cannot be replenished easily. It takes several million years to form [1][7].

![Figure1-2 Stages in the formation of coal](Source: Colorado geological survey)

Coal excavated from mines is often washed to improve its environmental performance as it contains materials like clay, sulphur, sand and trace elements. The ash content produced by coal burning is reduced to 50% by clean washing the coal which results in improved thermal efficiencies and lower carbon-di-oxide emissions and also low sulphur -di-oxide emissions. Cleaning coal by washing prepares it according to the customer specification and also reduces the emissions when used. Although mining, transportation and cleaning of coal causes serious environmental impacts such as acidic drainage, water quality, slurry impoundment stability, road damage due to heavy weight of trucks, physical disturbances and gob fires [7].
1.2.1.1 Use of coal for power generation

In modern day life coal has been put too much use to produce electricity. About 90% of United States coal production is converted to produce electricity. Coal is also used for various industrial purposes, used in steel industries and also for residential purposes. In electric-power plants thermal coal is used to produce electricity. Previously lump coal was used in power plants to produce steam. Today coal is first pulverized or crushed to fine powder in order to increase the surface area which helps in burning it quickly. This is called pulverized coal combustion system. This crushed coal is then added to a high temperature boiler or the combustion chamber and burnt. This heat produced is used to stem the water flowing from the pipes lining the wall of the combustion chamber. The pressure is used to generate electricity by turning giant turbines [2-7].

![U.S. Coal Usage](image)

Figure 1-3 US percentage of coal usage for various purposes

(Source: American geological institute)
1.2.1.2 Impacts due to combustion of coal

Coal contains elements which when burned at high temperatures such as in pulverized coal power plants form oxides of the same elements and are released into the atmosphere as emissions. The range and intensity of the environmental concerns occur due to the airborne emissions vary depending on the type of coal used, its shape, size, technology used to generate power and also the place where the plant is set up [6-8].

Sulfur-di-oxides, nitrogen oxides, particulates, trace elements such as mercury and greenhouse gas such as carbon di oxide are few airborne emissions which are released into the atmosphere due to combustion of coal in a coal power plant [8].

Currently 67% of sulfur dioxide emissions are caused due to burning of coal to generate electricity [7]. The sulfur present in the coal forms sulfur dioxide by combining with the oxygen present in the furnace. When these sulfur dioxide emissions are released into the atmosphere, it reacts with the water vapor to form sulfurous acid which oxidizes to form sulfuric acids which are components of acid rain. Nitrogen oxides also contribute to acid rain by forming nitric acid when released into the atmosphere.

Nitrogen oxides also are responsible for the formation of the ground level ozone which causes smog. Acid rain causes damage to the crops, forests, weathering of monuments, increase in the acidic content in the lakes and also health problems such as problems in visibility, asthma etc. this increased environmental and health problems due to acid rain called for a clean air act amendment by the federal government which mandated the reduction of So₂ emissions all over the nation [10-13].

Particulate emissions are solid or liquid particles present in the air which are responsible for occurrence of smog. These emissions are released due to burning of fossil fuels. These also cause health problems such as respiratory problems, problems in
visibility. Trace elements such as arsenic, selenium, mercury are released into the atmosphere due to combustion of coal. These trace elements can be removed by a number of technologies to limit their percent [7-8].

1.2 Flue gas desulfurization

Combustion or Burning of fossil fuels such as coal or oil to produce electricity is the main source of flue gas. Flue gas is a gas which is released into the atmosphere through a long chimney or duct pipe. These flue gases are released from a very high chimney or pipe because the composition of such gases is very different from that of normal atmospheric air composition. This flue gas is mainly formed due to the combustion of fossil fuels at coal fired power plants. The burning of fossil fuels causes serious environmental problems. There are a lot of combustion processes which produce flue gas as the final end product either to produce steam, heat or electricity. Combustion, gasification, pyrolysis and incineration etc. are some of the processes which produce flue gas to attain the right temperature needed or to produce different by-products [15-16].

Figure 1-4 coal burning power plant (USGS)
As we know in most of the countries worldwide fossil fuels are used for the production of electricity. Mostly coal is major fossil fuel which is been use for a very long time which has been used for the production of electricity.

![Figure 1-5 percentage of electricity generated by fuel type](Image)

(Source: U.S Energy Information Administration (EIA))

1.3.1 Composition of flue gas

The composition and the components of the flue gas depend on the type of substance being used. The flue gases produced from a fossil fuel power plant are our main concern. These fuel gases make the major contribution for the atmospheric pollution. The composition of what contains in the flue gas depends on the type of substance that is being used. That substance can be either a solid or a liquid. But the basic composition of flue gas from a power plant contains particulate matter, sulfur oxides, nitrogen oxides, carbon di oxide and carbon monoxide. They may also contain
heavy metals like arsenic, selenium and hydrocarbons if the temperatures are very high [21-24].

Figure 1-6 percentage of air pollution by sector in U.S (Source: NRDC and USEPA)

The flue gas from the coal fired power plants mainly consists of sulfur oxides, nitrogen oxides, particulate matter, carbon monoxide, carbon dioxide and trace elements. These components cause environmental pollution and also cause a variety of health problems. Therefore understanding these components and the effects which they pose to the environment is very useful in finding the effective solutions for the treatment before released into the atmosphere [22-23].

Sulfur present in the coal is converted to sulfur dioxide when it is burned. Sulfur dioxide is a toxic gas. The conversion to sulfur dioxide occurs due to the presence of oxygen and under normal conditions. When too much of oxygen is present in the flue gas the sulfur dioxide converts to sulfur trioxide (SO₃). Sulfuric acid is also formed (H₂SO₄). These cause acid rain which is very serious health problems when it combines with the rain droplets. Acid rain also causes damage to the building[22-23].
Coal also contains hydrocarbons. They are present in coal naturally. When the combustion process is incomplete they are released into the air. Methane and butane are some of the compounds which come under this category. Dust or soot is also present in the flue gas due to the combustion of coal. Dust or soot contains small particles which are very harmful because they may be toxic. Oxides of aluminum and calcium are present in the dust [21-24].

![Figure 1-7 percentages of gaseous components released into the atmosphere](Source: USEPA)

Oxides of nitrogen are of another concern to the environment due to their toxic behavior. The nitrogen present in the coal and the oxygen in the combustion process combine to form nitric oxide (NO). The nitric oxide again combines with the already present oxygen in the chimney to form nitrogen dioxide (NO₂). Nitrogen dioxide is very harmful that it contributes to the formation of ozone.

Carbon dioxide and carbon monoxide are also released during the combustion of coal. These are mainly the greenhouse gases responsible for the greenhouse effect [21-24].
1.3.2 Flue gas desulfurization process

Combustion of fossil fuels such as coal releases sulfur dioxide into the atmosphere. This sulfur dioxide has very harmful effects on both the health of human beings and the environment. Sulfur dioxide causes respiratory and breathing problems. If the sulfur dioxide is too dense due to the presence of particulate matter then it causes dense fog and reduces the visibility range. Apart from the health problems sulfur dioxide also causes acid rain. Acid rain as we know is very harmful as it contaminates the lakes, rivers, trees and also the agricultural crops. Coal is the main source for the electricity production globally. When coal is burned in coal fired power plants it releases almost 95% of sulfur present is the coal and is then converted to sulfur dioxide due to contact with oxygen[22].

Flue gas desulfurization typically known as FGD process is widely used process for the removal of SO$_2$ which is emitted into the atmosphere from the coal fired power plants. There are few more cleaning processes which are used for the reduction or removal of SO$_2$. But over the years the FGD processes have proved to be efficient in showing phenomenal results in the removal of sulfur dioxide [22]. The FGD processes are basically divided into two types: wet and dry. But the wet and the dry FGD processes have various ways of injecting the sorbent which is primarily the main constituent of the whole FGD process in removing the sulfur dioxide [22-24].
The basic theory behind the flue gas desulfurization process is simple chemistry. The sulfur dioxide emitted is acidic in nature. In order to neutralize the acidic sulfur dioxide gas alkaline reagents are used as scrubbers in the flue gas desulfurization processes. These reagents are sprayed or some way brought in contact with the sulfur dioxide. Then the gas is either absorbed or neutralized by the alkaline reagent. Slurry or a waste product is formed at the bottom of the tower. The reagents used vary depending on the system being used and also the cost. Generally two typical alkaline reagents used are lime or limestone [22-28][40].

The flue gas desulfurization processes are typically classified into two systems depending on the handling of the generated waste products. In the Once through or Non-regenerable systems the end product is either disposed of as waste or is processed to produce a by-product. In the regenerable systems the end product is again regenerated.
into the process to be again used as scrubbing reagent. Both the once-through and the regenerable systems have their pros and cons, but at present the costs involving in the setup of regenerable systems is higher than the once through systems [22].

The once-through and the regenerable systems are again sub-divided into wet, dry and semi-dry systems. The classification is done based on the form of the sorbent added, either dry or wet.

1.3.2.1 Types of Flue gas desulfurization systems

1.3.2.1.1 Wet FGD systems

The most common of all the three systems are the wet systems in which the sorbent is added in the form of aqueous slurry. There are few designs of wet FGD systems which provide maximum removal efficiency. Spray towers, venturi scrubbers and packed bed scrubbers are a few types of wet FGD systems. Of all the designs available, spray towers are the most extensively used. The liquid-gas ratio and the residence time of the sorbent in the tower are the two main considerations for design of various scrubbers [22-24][27].
The liquid-gas ratio is the ration between the amount of sorbent added to a certain ratio of gas being treated. The more the liquid-gas ratio means the sorbent added is more. The more the sorbent added the more efficient is the removal efficiency of sulfur dioxide [22]. Limestone and lime are two basic materials used as sorbents. The efficiencies of limestone and lime are nearly the same. But the cost of limestone is cheaper than that of the lime. Based on the removal efficiencies required and also the depending on the sulfur content present in the coal the type of sorbent can be chosen. The more the L/G ratio the more is the increase in the cost, because the more L/G ratio means increase in the sorbent percentage which ultimately increases the cost. Results have shown that the removal efficiency for limestone is 90% which is less than the
removal efficiency for the lime which is 95% [22]. The residence time is the amount of time the sorbent is in contact the gas treated.

Often the slurry which is formed at the bottom after the treatment is oxidized due to the presence of oxygen and forms scale[21-24][27]. This scale is usually a by-product called gypsum which is formed when limestone is used as the reagent scrubber. Scaling of the slurry at the bottom of the tank has been the main concern for years. The limestone forced oxidation is a wet FGD process which has shown significant results in reducing the scaling. In this process oxygen is forced into the reaction tank to form gypsum. The formed gypsum is removed and processed to use it as a by-product [22-27][40].

1.3.2.1.2 Dry FGD systems

In the dry FGD systems powered sorbent is directly brought in contact with flue gas. Since here the sorbent is used in its dry form, dry waste is produced from this process. This dry waste formed can be removed from the flue gas when it passes through particulate matter cleaning devices such as electrostatic precipitators or bag houses. Semi-dry systems uses lime slurry as the absorbent. But the water used in the lime slurry usually evaporates due to high temperatures. Spray dryers are usually used for semi-dry systems. The lime slurry is sprayed through sprayers before the flue gas enters the cleaning devices such as the bag houses or electrostatic precipitators[22-28].
The advantages of using dry FGD systems is comparatively more than the wet FGD systems. The disposal and handling of end waste products is easy. The cost of the sorbent reagents used in the process is also less. The dry FGD processes also do not require water. But the removal efficiencies which are our main concern to meet the regulations is offered more by the wet FGD systems. The removal efficiencies are more than 90% for wet FGD systems when compared to 50-60% of dry FGD systems [22].
1.4 Treatment techniques for wastewater from FGD systems

Flue gas desulfurization is a technique used to remove the SOx from the gases released from the coal fired power plants. The flue gas desulfurization systems are usually Wet systems, Dry systems and semi-dry systems. Wet FGD systems are more efficient in removing the Sox from the flue gas and have been very efficient in achieving 90-95% of removal efficiencies. In order to achieve the required emission controls and also the cost of the process, wet FGD systems have been the first choice for the removal of sulfur dioxide emissions.

The wastewater produced from these FGD systems is very complicated in nature and also very difficult to treat. In the wet FGD systems, the flue gas is treated by using lime slurry. So the slurry not only contains the sulfur oxides, it also absorbs the heavy metals, chlorides and particulate matter which are present in the flue gas. These contaminants are also present in the slurry which is formed at the bottom of the boiler. The slurry is acidic in nature [22-26]. So in order to prevent the corrosion of the surrounding system materials, certain amount of water is circulated through the system. This circulated water is acidic in nature, it contains heavy metals like mercury, arsenic, selenium and also contains particulate matter. There can be many reasons for the occurrence of all these contaminants in the circulated water or the water from the FGD systems. The type of coal, the efficiency of the bag house or the electrostatic precipitator used to clean the particulate matter, the reagent or the scrubber used in the FGD process and also the type of FGD systems being used [22-30].

The water from the wet FGD system has to be treated before it can be discharged. The concentrations of the contaminants present in the FGD wastewater have to meet the regulations of both state and the federal governments. There are certain
limits on mercury, selenium and arsenic. These few metals or trace elements are treated more strictly due to the harmful effects.

Table 1-1 EPA regulation limits for the potential pollutants in FGD wastewater

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Regulation limits</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg</td>
<td>10 ppt</td>
</tr>
<tr>
<td>Se</td>
<td>10 ppt</td>
</tr>
<tr>
<td>As</td>
<td>8 ppb</td>
</tr>
<tr>
<td>Cr</td>
<td>50 ppb</td>
</tr>
<tr>
<td>Cd</td>
<td>8 ppb</td>
</tr>
<tr>
<td>Cu</td>
<td>8 ppb</td>
</tr>
</tbody>
</table>

The treatment options available for Flue gas desulfurization water are:

- Physical-chemical treatment: the physical-chemical treatment is basically a precipitation process. The metal or the contaminant concentrations are reduced by precipitating them. Hydroxide, sulfide or carbonate precipitation process is used. First the pH of the wastewater is adjusted. There are two clarifiers in the treatment plant. In the primary clarifier hydroxide precipitations occurs along with the addition of coagulant. And in the secondary clarifier either the carbonate or the sulfide precipitation occurs. This treated water is then filtered and then discharged [35-40].

- Biological treatment: The biological treatment is used to remove the BOD and also the selenium. The treatment process can be either aerobic or anaerobic or both. Usually both the treatment process is installed. In the aerobic tank, the bacteria are used to reduce the BOD and in the anaerobic tank, the bacterium
reduces the selenium percentage by converting it into elemental selenium which is very easily removed by precipitation [35-40]

• Constructed wet lands: The constructed wet lands systems are very environmental friendly. There is no use of chemical compounds. There are series of wet lands cells and aeration cells. In these cells, plants and microorganisms are used to remove the metals. In the wet land cells plants and microorganisms are used to reduce metals and in the aeration cells oxygen is introduced so the iron oxidizes and can help in the precipitation of other metals and will be able to remove them from the wastewater [35-40].
**1.5 Activated carbon**

Activated carbon is a processed carbon to obtain more surface area for adsorption or filtration. Carbon is the main constituent of activated carbon. It also contains other heteroatoms such as hydrogen, oxygen, sulfur and nitrogen depending on the type of raw material used to prepare activated carbon. Coal, wood, nutshells are some of the raw materials which are used for making Activated carbon. Pyrolysis of carbonaceous materials is used to prepare activated carbon [41-42]. The process involves two steps: carbonization and activation. In the first step the whatever the raw material used is carbonized at temperatures lower than 800°C and in the second step activation of the carbonized material take place at temperatures between 950-1000°C. At the end of activation process a product with very high surface area is formed due to the irregular arrangement of carbon atoms during the pyrolysis [43]. There are two major types of activated carbon which are Granular activated carbon (GAC) and other is powdered activated carbon (PAC). Powdered activated carbon was the form of activated carbon which is first produced on industrial scale in the beginning of 20th century.

Activated carbon is been in use by ancient Hindus and the Egyptians for various purposes. Activated carbon is used widely because it is very economical and also it doesn’t affect the water being treated and doesn’t leave any taste or color. Activated carbon is also used in other water treatment units such as reverse osmosis or ion exchange to help control any damage caused by the water being treated. Since it is very economical and also been in use for many purposes its production also increased [44].

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Figure 1-11 Structure of activated carbon
1.5.1 Use of Activated carbon

Activated carbon has wide applicability in Environmental field. It is mainly used for adsorption and filtration. Granular activated carbon is used to adsorption process to remove organic and residual constituents from surface water, groundwater and wastewater. Activated carbon is used in food processing, biogas purification, removal of sulfur containing toxins, and also soil improvement [44].

Today drinking water is treated not only to remove taste or color or odor but also the organic and the inorganic waste present in it. From a long time water is being treated with various disinfectants to make it even safer to drink or use. But the chemical disinfectants used may leave residues that can be formed during the process and leave by-products which are very harmful for health. Synthetic organic compounds are present in water due to releasing of wastewater from the industries without treating [44]. Increase in the use of fertilizers also pollutes the surface waters. PAC and GAC are used in drinking water treatment equally. But usage of PAC in filtration process is less when compared with GAC because of the particle size.

Industrial wastewater is widely treated with activated carbon due to the strict regulations that has to be followed. Activated carbon is used as either a unit process after coagulation or filtration or it can also be used to remove toxic substances before the biological treatment. Activated carbon is also used in the remediation of soil to treat the ground water either by adsorbing or air stripping. Ground water is polluted either by industrial spills or over use of fertilizers. Organics present in water are removed by adsorption process. Adsorption occurs due to the presence of exert forces. The forces between the activated carbon surface and the contaminant are stronger than the contaminant and the water. Activated carbon is also a reducing agent as it removes the residual disinfectants present in the water [44-46].
1.5.2 Properties of activated carbon

Adsorption, reduction and catalysis are some of the functions of activated carbon. Adsorption is accumulation of any substance on the surface. As we know activated carbon is well known for the adsorption of wide range of substances such as organics, hydrocarbons, acids, surfactants, heavy metal ions. Activated carbon is also used to remove residual chlorine from water by transferring the electrons onto chlorine which is also known as reduction. Due to the large surface area of activated carbon it can use for catalysis. Its surface area can be used to impregnate certain catalyst to improve the functioning of activated carbon [44-46].

Particle size is main concern in selecting the activated carbon for an application. Even though the particle size is given on the marketed activated carbon, the particles are not of the same size. Depending on the particle size the adsorption depends. The percent of adsorption increases with the increase in the molecular weight. pH also affects the adsorption of substances onto the activated carbon surface. If the pH increases more activated carbon is needed to remove the contaminants. The level of concentration of the contaminant should be high so that the adsorption occurs successfully. For best results to be seen the contact time between the activated carbon bed and the contaminant has to be increased. The activated carbon bed should be packed properly in order to have more contact time [44].
Chapter 2

2.1 Introduction

This research focuses mainly on the development of a new treatment method for wastewater from flue gas desulfurization system. As mentioned earlier, the need for the treatment of the wastewater from FGD system is important as it is very complicated in nature and also contains very high percentages of heavy metals and trace elements. Methods like physical chemical treatment, biological treatment and wet lands are being used at present. These methods, as stated earlier, require more space in order to be setup, chemicals are used in order to remove certain elements and them only reduce certain selected metals rather than having an impact on all the metals.

In this thesis we are trying to apply the activated carbon to the FGD wastewater to reduce the concentration of few metals which are very harmful and have to be maintained at concentrations as guided by the NPDES and the EPA.
Table 2-1 priority pollutants and their potential environmental concern

<table>
<thead>
<tr>
<th>Priority pollutant</th>
<th>Environmental concern</th>
</tr>
</thead>
<tbody>
<tr>
<td>Selenium</td>
<td>Observed in very high concentrations in the FGD wastewater, causes changes in the aquatic life, can cause damage to the nervous system, liver and kidney.</td>
</tr>
<tr>
<td>Mercury</td>
<td>Exposure can cause metabolic changes and damage to liver and kidneys.</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Causes damage to the fish life and also can cause cancer in humans.</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Causes tissue damage and organ abnormalities</td>
</tr>
<tr>
<td>Chromium</td>
<td>It is observed in high concentrations in the groundwater receiving the coal combustion water, can cause changes in the metabolism and may affect the growth.</td>
</tr>
<tr>
<td>Lead</td>
<td>It causes serious damage to the brain, kidneys, nervous system and also red blood cells.</td>
</tr>
<tr>
<td>Copper</td>
<td>Changes in the metabolism and growth</td>
</tr>
<tr>
<td>Boron</td>
<td>Exposure causes nausea, diarrhea and is toxic for vegetation.</td>
</tr>
</tbody>
</table>

2.2 Methodology

The whole experimental procedure is done in three stages. First the preparation of iron impregnated and ZVI activated carbon and secondly batch tests are run for 300 samples. Finally the treated water samples are analyzed by ICP-MS to know the reduced concentrations of the desired metals.
The FGD wastewater is provided by the luminant company. The wastewater is discharged from a wet FGD system. In this experiment activated carbon of three forms has been used. From the previous studies it is very much clear that the activated carbon has proven to adsorb the metals and reduce their concentrations. Activated carbon has been used for the treatment of wastewater for ages. We also know that activated carbon is modified to improve its qualities to adsorb certain targeted metals. In this research the activated carbon is modified in two types. One is the iron impregnated activated carbon and the other is the zero valent iron activated carbon. The preparation procedure for both the form has been previously developed by choi (2008). The same procedure has been used here in this research.

The stages of the experiment are shown in the form of a flow chart.
The activated carbon (HD 3000) is first washed and then dried at room temperature. The dried activated carbon is then impregnated with iron through the impregnation method. 22.8 g of ferric nitrate is melted with 5 ml water and is then added to 10g of the dried activated carbon. The slurry is then dried at room temperature and
then ramped at 60-70°C for 2 hours and then again ramped at rate of 180 °C/h to 150°C for 1 hour. This is done to remove any moisture. Then it is again ramping is increased to 300°C and this temperature is held for 4 hours. At this stage any nitrate ions that are present are removed. Then it is allowed to cool.

Figure 2-3 the activated carbon used for all the research tasks and the muffle furnace which is used to prepare the GAC-Fe.

The iron impregnated activated carbon is used to prepare GAC-ZVI. The reduction to elemental iron is done by using NaBH4 solution. The GAC-Fe is added with methanol
and DI water and then the NaBH₄ solution is added drop by drop to the GAC-Fe slurry. The NaBH₄ solution is added drop by drop and is stirred. This procedure is performed very carefully due to any production of explosive H₂. The iron impregnated GAC has the color of rusted iron and the GAC- ZVI has a shiny black color. The GAC-ZVI has to be stored properly.

Figure 2-4 Three different forms of Granular activated carbon: GAC, GAC-Fe AND GAC-ZVI prepared and used in the experiment.

For the batch experiment to be conducted, the GAC, GAC-Fe and GAC-ZVI are added into the sample bottles. The amount of the GAC to be added is different for each bottle. For a certain time interval the amounts of GAC are in the increasing order. The GAC is added to the bottles and the FGD wastewater is first filtered to remove any solid particles that are present. 20 ml of the wastewater is added to the GAC. The following table will give more information on the sampling amounts of GAC and the time intervals.
<table>
<thead>
<tr>
<th>Time interval</th>
<th>Amount of GAC/GAC-Fe/GAC-ZVI (g/L)</th>
<th>Amount of GAC/GAC-Fe/GAC-ZVI (mg/20mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 min</td>
<td>0.75</td>
<td>15</td>
</tr>
<tr>
<td>5 min</td>
<td>1.50</td>
<td>30</td>
</tr>
<tr>
<td>20 min</td>
<td>2.15</td>
<td>43</td>
</tr>
<tr>
<td>1 hour</td>
<td>3.5</td>
<td>70</td>
</tr>
<tr>
<td>4 hour</td>
<td>4.5</td>
<td>90</td>
</tr>
<tr>
<td>10 hour</td>
<td>5.5</td>
<td>110</td>
</tr>
<tr>
<td>24 hour</td>
<td>6.5</td>
<td>130</td>
</tr>
<tr>
<td>48 hour</td>
<td>7.5</td>
<td>150</td>
</tr>
<tr>
<td>72 hour</td>
<td>8.75</td>
<td>178</td>
</tr>
<tr>
<td>96 hour</td>
<td>10.00</td>
<td>200</td>
</tr>
</tbody>
</table>

So for every form of GAC, GAC-Fe and GAC-ZVI there 100 sample each. A shaker is used to keep the water and the activated carbon in motion so that there is movement of water and all the water get in contact with the GAC. The speed of the shaker is kept very low so that the activated carbon doesn’t get disturbed too much and break into smaller particles.
Figure 2-5 Shaker used during the Batch tests

Figure 2-6 The right most is the picture showing the batch experiment, the second shows the filters used to remove any fine particles of the GAC and the third showing the final 300 treated water samples to be analyzed.

From the 20 ml treated water 6 ml sample is taken. The water treated is then again filtered using 0.45µm filters to remove the finer particles of GAC. The water is again filtered to remove any small particles of activated carbon that may be present in the
water. These samples are then analyzed using the inductively coupled plasma-mass spectroscopy (ICP-MS) to know the concentrations of the metals that are targeted. ICP-MS is used to measure the concentrations of metals and several non-metals in the water lower than part per trillion.

2.3 Summary

This chapter provides the information and summarizes the experimental method and procedure in detail. The procedure for the preparation of the GAC-Fe and the GAC-ZVI are described in detail. The flow charts and the photographs illustrations give an overall picture of the whole experimental procedure. The test results obtained from the ICP-MS analysis is presented in the next chapter and is followed a detailed analysis and discussion of the test results.
Chapter 3

Results and discussions

3.1 Introduction

The FGD wastewater is very complex in nature. The composition of FGD wastewater depends on lot of factors, type of coal used, the rank of the coal, the type of FGD system used and also the particulate matter removal efficiency. The processes in use for the FGD wastewater treatment are very tedious to perform due to the use of chemical compounds for the treatment. They require ample amount of space to be installed and also the wastes produced from these processes have to be handled.

In this study GAC impregnated with iron and GAC impregnated with zero valent iron are used to treat the FGD wastewater to reduce the concentration of selected regulated pollutants such as mercury, arsenic, selenium, lead, copper and chromium. Adsorption batch experiments are conducted and then analyzed with ICP-MS to detect the metal concentrations. This chapter presents the ICP-MS results with their detailed analysis and discussion.

3.2 Properties of GAC/FeOx and GAC/ZVI.

We have used two forms of GAC in this experiment. GAC impregnated with iron and GAC impregnated with zero valent iron. Results from previous research had shown arsenic affinity towards iron modified GAC Chen et al (2007). Incipient wetness impregnation method was used to incorporate iron and ZVI onto GAC Choi et al (2009). Same process was applied in this work.
3.3 ICP-MS Analysis Results

Adsorption batch experiments are conducted to treat the FGD wastewater with GAC/FeOx and GAC/ZVI. The ICP-MS results showed reduction in the concentrations of the metal compounds after treatment with the GAC/FeOx and GAC/ZVI. The kinetics of the adsorption by GAC was promising for mercury, arsenic and lead. The concentrations of the metal compounds in the raw FGD wastewater are very high. The concentration of the metal compounds after the adsorption test is comparatively less. For the 10 different conditions of GAC/FeOx and GAC/ZVI used, we couldn't see any significant trend in the adsorption kinetics.

For the 10 different conditions of GAC/FeOx and GAC/ZVI, graphs were plot between concentration and time. Normalized concentration vs time plots were shown below for different metal compounds.
Figure 3-1 Adsorption kinetics of Hg: C/Co vs Time plot two conditions of GAC, GAC/FeOx and GAC/ZVI. Lowest condition: 1.5 g/L; Highest condition: 10 g/L
Figure 3-2 Adsorption kinetics of As: C/Co vs Time plot two conditions of GAC, GAC/FeOx and GAC/ZVI. Lowest condition: 1.5 g/L; Highest condition: 10 g/L
Figure 3-3 Adsorption kinetics of Pb: C/Co vs Time plot two conditions of GAC/FeOx and GAC/ZVI. Lowest condition: 1.5 g/L; Highest condition: 10 g/L
Figure 3-4 Adsorption kinetics of Cr: C/Co vs Time plot two conditions of GAC/FeOx and GAC/ZVI. Lowest condition: 1.5 g/L; Highest condition: 10 g/L
All the above graphs show the adsorption kinetics of the Batch test we conducted. Mercury and lead show a similar trend in the adsorption. Selenium concentrations have increased beyond the raw water concentrations, it can be because of the reduction of other metal compounds like arsenic, and mercury etc. may have caused significant increase in the selenium concentration. On the whole, the adsorption kinetics has shown results for which further study is required. The following table gives an overall explanation and performance of GAC, GAC/FeOx and GAC/ZVI for different metal compounds.

Table 3-1 Performance of GAC, GAC/FeOx and GAC/ZVI for different metal compounds.

<table>
<thead>
<tr>
<th>Metal compound</th>
<th>Overall performance</th>
<th>Order</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury (Hg)</td>
<td>Good</td>
<td>GAC&lt;GAC/FeOx&gt;GAC/ZVI</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>Average</td>
<td>GAC=GAC/FeOx&gt;GAC/ZVI</td>
</tr>
<tr>
<td>Selenium (Se)</td>
<td>Poor</td>
<td>GAC=GAC/FeOx=GAC/ZVI</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>Good</td>
<td>GAC&lt;GAC/FeOx=GAC/ZVI</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>Poor</td>
<td>GAC=GAC/FeOx&gt;GAC/ZVI</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>Good</td>
<td>GAC=GAC/FeOx&gt;GAC/ZVI</td>
</tr>
</tbody>
</table>
From the whole experiment two conditions, where the amount of GAC/GAC-Fe/GAC-ZVI used are low and high. At both these conditions the removal efficiencies of the metal compounds are calculated.

Condition 1: low amount of GAC-GAC/FeO$_x$-GAC/ZVI

Table 3-2 removal efficiencies of metal compounds at low amount of adsorbent

<table>
<thead>
<tr>
<th>Metal compound</th>
<th>GAC</th>
<th>GAC/FeO$_x$</th>
<th>GAC/ZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>95%</td>
<td>96%</td>
<td>98%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>85%</td>
<td>71%</td>
<td>46%</td>
</tr>
<tr>
<td>Lead</td>
<td>37%</td>
<td>78%</td>
<td>89%</td>
</tr>
<tr>
<td>Copper</td>
<td>48%</td>
<td>*</td>
<td>66%</td>
</tr>
<tr>
<td>Chromium</td>
<td>77%</td>
<td>36%</td>
<td>74%</td>
</tr>
</tbody>
</table>

[* = experimental error]

In the above table, removal efficiencies for metal compounds at low amount of GAC/GAC-Fe/GAC-ZVI are shown. GAC-ZVI have shown better removal efficiencies for all the metal compounds except for arsenic for which GAC has more removal efficiency.
Condition 1: Higher amount of GAC-GAC/FeO$_2$-GAC/ZVI

Table 3-3 removal efficiencies of metal compounds at high amount of adsorbent

<table>
<thead>
<tr>
<th>Metal compound</th>
<th>GAC</th>
<th>GAC/FeO$_2$</th>
<th>GAC/ZVI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercury</td>
<td>98%</td>
<td>99%</td>
<td>97%</td>
</tr>
<tr>
<td>Arsenic</td>
<td>60%</td>
<td>47%</td>
<td>48%</td>
</tr>
<tr>
<td>Lead</td>
<td>86%</td>
<td>95%</td>
<td>87%</td>
</tr>
<tr>
<td>Copper</td>
<td>76%</td>
<td>87%</td>
<td>51%</td>
</tr>
<tr>
<td>Chromium</td>
<td>2%</td>
<td>85%</td>
<td>*</td>
</tr>
</tbody>
</table>

[*=experimental error]

In the above table, removal efficiencies for metal compounds at high amount of GAC/GAC-Fe/GAC-ZVI are show. GAC-Fe have shown consistent removal efficiency for all the metal compounds.

These removal efficiencies help us understand the behaviour of metal compounds and also their affinity towards the adsorbent. Not all metal compounds can have the same condition used for the removal or reduction, but the best suitable adsorbent and condition can be applied based on the requirement of wastewater treatment plant.
Chapter 4

Conclusion

This research is a preliminary work to apply the concept of GAC impregnated with iron (GAC/FeOx) and GAC impregnated with zerovalent iron (GAC/ZVI) to the FGD wastewater and to observe the adsorption kinetics. The GAC/FeOx and GAC/ZVI previously have shown good results on removal of metals in wastewater. We applied the two most used forms of modified GAC to FGD wastewater. Based on the results obtained, it can be deduced that there was significant adsorption of some metal compounds while certain metal compounds like selenium and copper did not respond to the experiment. We also observed a definite trend in the kinetics of all the metal compounds. The FGD wastewater is of very complex nature. The full details of the FGD wastewater are not known in depth. This work can be further done by using different forms of modified GAC and also based on the speciation of the metals. A two stage experimental procedure can be applied to see there is significant adsorption of metal compounds. There is scope for future work but on an extensive scale. Rigorous trial and error analysis has to be done using different forms of GAC to observe any significant reduction in the concentrations of metal compounds.
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Biographical Information

Manjira Kudaravalli was born in Gudivada, Andhra Pradesh, India on the 16th of November 1990. She received her bachelor’s degree from the S.R.K Institute of Technology which is affiliated to the Jawaharlal Nehru Technological University, India in April 2012. Author started her Masters in Civil engineering majoring Environmental engineering in fall (2012) from the University of Texas at Arlington. During the course of her study she worked as a student assistant in University center. The author’s present research is based on the preliminary work on adsorption of metal compounds in FGD wastewater using Iron impregnated activated carbon.