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UTILIZATION OF COKE AND FUNCTIONALIZED COKE-BASED COMPOSITE FOR UPTAKE OF HEAVY METALS FROM WASTEWATER

By

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Dissertation in fulfillment of the requirement for the degree

MASTER OF TECHNOLOGY

in

CHEMISTRY

in the

FACULTY OF SCIENCE

of the

UNIVERSITY OF JOHANNESBURG

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DEDICATION

This work is dedicated to my forever loving mom Miss Zehlile Virginia Zwane together with my aunts and all members of the family. I thank you for being the home base where I draw motivation.
I would like to thank God Almighty who sustained and carried me throughout the duration of this work.

I am thankful to my supervisors, Prof. SB Mishra and Prof. BB Mamba for providing invaluable insights, their sincere coaching, timely encouragement as well as their support in making this task successful.

I would like to give thanks to many people who helped me during the course of this study. The technical assistance provided by Mr Sacko Amoudjata, Mr Motlatsi Phali and Dr Alex Kuvarega is appreciated. Dr Hemant Mittal who was supportive and genuinely interested in this work is also acknowledged. I would like to extend my sincere thanks to the Metallurgy Department at UJ for providing their laboratory facilities.

My special thanks to Mcphail Coal Distributors in Isando Johannesburg for supplying the coke sample. I would also like to acknowledge Eskom Tertiary Education Support Program (TESP), Mintek Nanotechnology Innovation (NIC) and University of Johannesburg (Faculty of Science) for funding this work. Apart from all the efforts, the success of any project depends on the direction and inspiration of many others. I am thankful to my friends Nozipho Gumbi, Sania Kadanyo and Kholiswa Yokwana for insightful conversations and business lunches. Last but not least to all my family members Noluthando Kunene, Thando Zwane, Smangele Zwane, Siphindile Zwane, Nonkululeko Mthembu and Mrs Zanele Kunene for being a source of moral support and driving force to what I do.
PRESENTATIONS AND PUBLICATIONS

Conference attended


Publications


ABSTRACT

This study investigated the functionalization of coke particles and their utilization for the preparation of coke-polymer composite. Looking at the possibility of using it for the removal of lead and chromium ions from their aqueous solutions. Due to various inorganic materials in coke, it was treated with acid to demineralize the ash content. The demineralized coke was further oxidized with hydrogen peroxide to add functional groups on its surface as well as in the bulk of coke particles before coating of the polymers. The composite preparation entails modifying the surface properties of coke with hydrophilic polymers like polyvinyl alcohol (PVA), poly ethylene glycol (PEG) and poly vinyl pyrrolidone (PVP) followed by the crosslinking to improve the interfacial interaction between the polymer and coke to make the synthesized composite stable in water.

The structural composition of coke and modified coke was examined by FT-IR spectroscopy, X-ray diffraction, X-ray fluorescence, Raman Spectroscopy, thermal analysis and scanning electron microscopy combined with energy dispersive X-ray analysis. It was also observed that the modified coke samples have enhanced carbon reactivity which indicates that the non-carbon phases were removed by the treatment with acid.

The adsorption studies for the removal of Pb (II) and Cr (III) ions from contaminated water was done in batch mode using variables such as pH, contact time and the initial concentration. The synthesized material was found to have better adsorption capacity as compared to raw coke. To understand the adsorption isotherm processes, Freundlich and Langmuir isotherms were applied. The monolayer adsorption capacity for the removal of lead ions was found to be 2.41 mg/g, 2.95 mg/g, 8.32 mg/g, 9.70 mg/g and 9.84 mg/g for raw coke, acid treated coke, PVA coated coke, PEG coated coke and PVP coated coke, respectively. The chromium monolayer adsorption capacity was found to be 9.48 mg/g, 9.94 mg/g, 35.84 mg/g, 32.79 mg/g and 34.13 mg/g for the same order of adsorbents mentioned for lead. Studies were carried out at the optimum pH of 6.0 for both the metal ions. The adsorption kinetic studies showed that both the metal ions
followed pseudo second order rate equation and the adsorption equilibrium was attained in 60 minutes and 120 minutes for Pb (II) and Cr (III) ions, respectively.
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<tr>
<td>Abbreviation</td>
<td>Full Form</td>
<td></td>
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<tr>
<td>--------------</td>
<td>-----------</td>
<td></td>
</tr>
<tr>
<td>AAS</td>
<td>atomic absorption spectrophotometer</td>
<td></td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing Materials</td>
<td></td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
<td></td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FT-IR</td>
<td>fourier transform-infrared spectroscopy</td>
<td></td>
</tr>
<tr>
<td>FDT</td>
<td>final decomposition temperature</td>
<td></td>
</tr>
<tr>
<td>FC</td>
<td>functionalized/acid treated coke</td>
<td></td>
</tr>
<tr>
<td>FPEG</td>
<td>functionalized polyethylene glycol coated coke</td>
<td></td>
</tr>
<tr>
<td>FPVA</td>
<td>functionalized polyvinyl alcohol coated coke</td>
<td></td>
</tr>
<tr>
<td>FPVP</td>
<td>functionalized polyvinyl pyrrolidone coated coke</td>
<td></td>
</tr>
<tr>
<td>IDT</td>
<td>initial decomposition temperature</td>
<td></td>
</tr>
<tr>
<td>Met-coke</td>
<td>metallurgical coke</td>
<td></td>
</tr>
<tr>
<td>mg/g</td>
<td>milligram per gram</td>
<td></td>
</tr>
<tr>
<td>mg/L</td>
<td>milligram per litre</td>
<td></td>
</tr>
<tr>
<td>Pet-coke</td>
<td>petroleum coke</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>lead</td>
<td></td>
</tr>
<tr>
<td>PEG</td>
<td>polyethylene glycol</td>
<td></td>
</tr>
<tr>
<td>PVA</td>
<td>polyvinyl alcohol</td>
<td></td>
</tr>
<tr>
<td>PVP</td>
<td>polyvinyl pyrrolidone</td>
<td></td>
</tr>
<tr>
<td>rpm</td>
<td>revolutions per minute</td>
<td></td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
<td></td>
</tr>
<tr>
<td>USEPA</td>
<td>United States Environmental Protection Agency</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
<td></td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
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</tr>
</tbody>
</table>
CHAPTER 1
INTRODUCTION

1.1 Background and Motivation

Water is of great importance to economic growth and sustainable development of a nation. South Africa, like many other countries experiences water scarcity caused by agricultural water demand, unreliable rainfall, rapid industrial growth and more people moving to urban areas. It is therefore important to clean or treat water according to its required purpose of appropriate quality.

New approaches of water treatment methods are still under examination since it is the major challenge for municipalities and industries to dispose polluted water on a daily basis. Industrial wastes are the major causes of health hazards in water pollution.\(^1\) As a result, a number of researchers developed methods which involve filtration, ion exchange, membrane process, chemical precipitation, adsorption, etc for the removal of various pollutants like heavy metals in water.\(^2\) However, these methods have their individual limitations in practice. Among all these technologies adsorption is the most studied and has a wider applicability in contaminated water control.\(^2\)

Heavy metal ions in water originate from domestic and industrial activities (such as mining, smelting operation and agriculture). They are well described as metals with atomic density greater than 5 g/cm\(^3\).\(^3\) Some heavy metals (Cd, Pb and Hg) are found to be cumulative poison which do not break down easily in the environment whereas others (like Cd, Ni, and Pb) are said to be carcinogenic and mutagenic.\(^4\) Water pipes made from lead also contributes in the contamination of water with lead ions. They are frequently used because they are flexible to work with and do not rust.\(^5\) The accumulation of lead in the human body causes chronic poisoning which include mental retardation to infants and kidney problem to adults.\(^5\)
Mercury discharge is still classified as a major problem area in industries. Processes like volcanic activities are the cause of natural occurring mercury. It is capable of combining with other elements to form inorganic and organic compounds. The inorganic forms are the common compounds found in drinking water.\textsuperscript{6} Toxicity of mercury compounds depend on their species and the most toxic form is methyl mercury.\textsuperscript{7} This results in aquatic ecosystem when the bacteria methylate in organic mercury. The process occurs in water sediments when the pH is low and there are highly dissolved organic carbons. Mercury can cause damage to the brain, nervous system and kidneys in the human body.

Chromium and its compounds are widely used in industries and these industries produce large quantities of toxic wastewater runoff. The two common oxidation states of chromium in the environment are hexavalent Cr (VI) and trivalent Cr(III).\textsuperscript{8} For mammal metabolism traces of Cr (III) are essential since it is less toxic than Cr (IV). However, Cr (III) is likely to oxidize to Cr (IV) therefore environmental regulations set in the limit for the total chromium present in water.\textsuperscript{8}

Many studies have been done involving the adsorption of chromium on activated carbon prepared from different sources.\textsuperscript{9} Up to so long activated carbon is recommended as a major adsorbent for water treatment because of its modified surface, efficiency and being reliable. The disadvantage associated with activated carbon use is the high cost, especially in the industrial field where there are large effluents. A number of methods have been used for the removal of heavy metal ions on wastewater like adsorption with natural materials but these are very slow processes.\textsuperscript{10} The use of carbonaceous materials has been implemented for wastewater treatment and water purification due to their easy handling and operability.\textsuperscript{11} It has also been reported in literature the application of unmodified coke for the removal of heavy metals (Ag, Cd, Cu) for ternary and binary mixtures in aqueous solution.\textsuperscript{12} In the study it was found that coke has the ability to remove both Ag and Cu mixture however the adsorption capacity was low. Therefore chemical modification to improve the acidic functional groups can enhance the adsorption ability of coke to the cations is required.
Chapter 1: Introduction

1.2 Justification

Coke is one of the materials used as activated carbon precursor. It is preferred because of its high carbon content, low volatile matter and low ash content. With the increase of oil refining industries and demand of heavy oil processing, coke is becoming cheap and abundant in the market making it an economical motivation for wastewater treatment plants. Adsorption technology has been improved in many ways by polymer composites. In the present study, it is assumed that the polymer coating method should alter the surface properties of coke to form a versatile coke-polymer composite. This method avoids complicated polymerization reactions and enhances mechanical strength, wettability, conductivity and adsorption properties of the material. Incorporation of hydrophilic polymers to coke particles has been reported but to date no attempt has been made to study the coke polymer composite on the removal of heavy metals in aqueous solution.

1.3 Aim and objectives of the study

The aim of the study was to develop a coke polymer composite, with different polymers having water absorbing capacity (PVA, PEG and PVP) as an adsorbent that can be used in the removal of lead (II) and chromium (III) ions in aqueous solution. The objectives of the study were:

1. To determine the ability of raw coke for the removal of heavy metals (Pb^{2+}, and Cr^{3+}) from synthetic water.

2. To functionalize coke by wet oxidation methods.

3. To assess the ability of the functionalized coke on the removal of heavy metals.

4. To coat both the functionalized and non-functionalized coke with hydrophilic polymers (PEG, PVA and PVP) to enhance hydrophilicity of the composite.
5. To study the structural changes of coke before and after modification using scanning electron microscope (SEM), Brunauer-Emmet-Teller (BET), X-ray diffractometer (XRD), Raman Microscope and thermogravimetric analysis (TGA).

6. To test the performance of functionalized coated coke for heavy metals removal using flame atomic absorption spectroscopy (FAAS).

1.4 Outline of the dissertation

The brief summary of the contents of this dissertation are as follows:

Chapter 1

Introduction is outlined in this chapter with the brief overview of problem statement, justification, aims and objectives of the study together with the research framework.

Chapter 2

This chapter gives the overview of the study impact and literature review on coke modification, origin and applications. The effects of heavy metals in the environment as well as water treatment techniques are discussed in this chapter.

Chapter 3

This chapter details the experimental procedures on coke modification and characterization using various characterization techniques.

Chapter 4

In this chapter, the preparation procedures for the coke-polymer composites are presented and discussed with relevant characterization techniques adopted.
Chapter 5

In this chapter the application of parent coke together with the coke-polymer composites in the removal of lead and chromium metals from aqueous media is presented. The adsorption processes on different experimental parameters and implication of adsorption isotherms are also discussed.

Chapter 6

This chapter gives highlights on roles of minerals found in coke on the removal of lead and chromium ions from aqueous solution.

Chapter 7

The overall conclusion and future work recommendations are presented in this chapter.
Chapter 1: Introduction

1.5 References


6. Mercury in drinking water: Division of environmental and occupational health consumer and environmental health service.


CHAPTER 2
LITERATURE REVIEW

2.1 Introduction

This chapter presents the relevant literature on the use of carbonaceous materials as alternative adsorbents in water treatment. Insight of the technologies used for the removal of heavy metals in aqueous solution as well as the advantages and disadvantages associated with these techniques are discussed. In this section, the origin of coke as well as its application is discussed. Challenges associated with the presence of heavy metals in aqueous solutions are also addressed.

2.2 Heavy metals in water

Heavy metals always find a way to get into our water streams as a result of their soluble nature in the aquatic environment. There are a large number of metals which exceed the atomic density of 5 g/cm$^3$ indicating heavy metals.$^1$ Some of the relevant ones in the environmental context are listed in Table 2.1. These heavy metals are classified as hazardous metals because they tend to bioaccumulate with time and they are poisonous. As a result of their harmful effects, permissible limits are set by the United States Environmental Agency (USEPA) to meet the quality of water.$^2$

2.2.1 Separation techniques for the removal of heavy metals in water

2.2.1.1 Chemical precipitation

The most common applied precipitation methods for metals are hydroxide and sulphide precipitation. Depending on the metal of interest other methods like carbonate and sulphate precipitation are also employed. Hydroxide is the frequently used precipitation method whereby chemically complex compounds are
not involved by using lime.\textsuperscript{3} The disadvantage associated with the use of lime is its low solubility and with that the dosing system needs to be sensibly designed.\textsuperscript{4}

**Table 2.1: MCL standards for hazardous metals and effects on human.\textsuperscript{2}**

<table>
<thead>
<tr>
<th>Toxic metal</th>
<th>MCL(mg/L)</th>
<th>Industry</th>
<th>Toxicity</th>
</tr>
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<tbody>
<tr>
<td>Lead</td>
<td>0.06</td>
<td>Ceramic, glass and battery manufacturing industries</td>
<td>Fetal brain damage, biosynthesis disruption, rise of blood pressure and kidney damage</td>
</tr>
<tr>
<td>Chromium</td>
<td>0.05</td>
<td>Electroplating, milling and etching</td>
<td>Carcinogenic, nausea, vomiting and headache</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.01</td>
<td>Fertilizer, photoconductor production, battery and electroplating</td>
<td>Central nervous system damage, loss of smell and kidney damage</td>
</tr>
<tr>
<td>Copper</td>
<td>0.25</td>
<td>Vehicles, paper mills, fertilizer, petroleum refineries and conductors</td>
<td>Stomach-aches, insomnia and liver damages</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.2</td>
<td>Metal plating, mining, production of paints and pigments</td>
<td>Coughing, chronic asthma and skin irritation</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.05</td>
<td>Natural rock formation and activities such as mining and smelting ore</td>
<td>Affects nervous system, kidney and cause various forms of cancer</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.8</td>
<td>Steel industries for corrosion prevention</td>
<td>Depression and increase in thirst</td>
</tr>
</tbody>
</table>

On the other hand sulphide precipitation involves the use of sulphides with metal ions to form an insoluble sulphide metal. This method is said to be more effective
than hydroxide precipitation as it can achieve low metal solubilities.\textsuperscript{3} The most reliable method in sulphide precipitation is the usage of slightly soluble sulphide precipitation (SSSP) process (prepared by reacting FeSO\textsubscript{4} and NaHS). This method prevents the production of H\textsubscript{2}S odour.\textsuperscript{4} The main drawback with chemical precipitation is the remaining solid residue and difficulty on low concentrations treatments (less than 250 mg/L).\textsuperscript{5-6}

2.2.1.2 Electrodialysis

Electrodialysis is a process where a semi permeable ion-selective membrane is used to separate the ionic components in a continuous or a batch mode. The general problems with electrolysis process are concentration polarization and membrane scaling.\textsuperscript{7}

2.2.1.3 Ion exchange

Ion exchange is another method used for the removal of heavy metals. It is mostly used in the metal finishing industry to remove dissolved heavy metals.\textsuperscript{8} This is a reversible process where ions in a feed are exchanged with similar charged ions on the solid surface of a resin.\textsuperscript{3} When ions of the resin are completely exchanged, the resin is taken out for regeneration which leads to high operation costs.\textsuperscript{9}

2.2.1.4 Coagulation and flocculation

This technique can also be used for the treatment of wastewater laden with heavy metals. Technically; on a coagulation process, the colloidal particles are destabilized through the addition of a coagulant which that is followed by flocculation to increase the particle size of the unstable particles.\textsuperscript{10} The limitations associated with this technique is the consumption of too many chemicals leading to the production of the toxic sludge. The produced sludge needs to be again stabilized to prevent the heavy metals from leaking into the environment.
2.2.1.5 Adsorption

Adsorption simply involves the transfer of soluble substances in solution into a suitable solid surface and bound on by physical or chemical interactions. This method is regarded as the effective technique which is able to decontaminate water without leaving behind toxic degraded products and its simplicity. With trust and reliability on adsorption our laboratory worked on studies using this method for heavy metals removal from aqueous solution on lignocellulosic fiber–ethylene vinyl acetate, clinoptilolite-polypropylene and EVA/polycaprolactone-bentonite composites. Although this technology is well established the focus on inventing potential, well suitable, reliable, and cost effective adsorbents is still on going.

2.3 Carbonaceous materials

2.3.1 Description of carbonaceous materials

The term carbonaceous defines a substance that is rich in carbon. It generally covers a large number of products such as coal, coke, coconut shells, wood, peat, activated carbon, carbon nanotubes etc. These are solid substances with massive or with large volume of combustibles depending on its nature. Functional carbonaceous materials have a variety of applications which include their use as adsorbents, catalysts electrode materials etc. as indicated in Figure 2.1.
2.3.2 Modification of carbonaceous materials

The idea of carbonaceous materials modification is an attractive path towards its novel applications. Due to versatility of these materials they can be converted or available as crystalline, amorphous, nanostructured, activated and functionalized. There are numerous ways to alter or incorporate functionality on carbonaceous materials in order to extend their practical applications. Few methods are briefly discussed below:

(i) Acid treatment – Non-oxidants acids like HCl and HF are frequently used to remove mineral matter present in a carbonaceous material. This process alters the surface area as well as the pore texture of the material since the mineral matter is said to block some parts of carbon porosity.
(ii) Surface oxidation – Oxidation could be carried out in a gas or a liquid phase to increase the concentration of oxygen containing functional groups (such as lactone, phenol, carboxyl and quinone) on the carbon surface. It has been investigated that gas oxidation mostly enhances the concentration of hydroxyl and carbonyl surface groups whereas the liquid phase oxidation favors the carboxylic acid groups. The oxidation ability strongly depends on the strength of the oxidants, which include oxidizing gases (air, oxygen, ozone, nitrous oxide, nitric oxide) and oxidizing solution (like nitric acid, sulphuric acid, hydrogen peroxide, hypochlorite, permanganate and dichromates). The main purpose of surface oxidation is to produce more anchoring sites for additional surface groups and structural manipulation, therefore care must be taken during oxidation to prevent more harsh conditions that may lead to deterioration and structural breakdown of the carbon framework.

(iii) Thermal treatment – Alteration of carbonaceous materials via thermal treatment could be of KOH, carbon dioxide and microwave treatment. Heat treatments also occur in an inert environment where gases such as hydrogen, argon and nitrogen are used in order to remove hydrophilic surface functionalities and hydrogen gas has been found to be more effective in terms of stabilizing the hydrophobic nature of the carbon at 900 °C. When a carbonaceous sample was physically mixed with KOH at an elevated temperature (750 °C), the surface area and pore volume increased. Similar changes were obtained when carbon dioxide was treated with the sample at 950 °C. Microwave treatment is regarded as a rapid, precise temperature control and minimal energy consumption method. In the regeneration of activated carbon prepared from coconut using microwave, the adsorption rate was increased as a result of microwave irradiation modified the pore size distribution as well as the surface chemistry of activated carbon.

(iv) Nanoparticles attachment – A simple way of incorporating a secondary phase on a carbonaceous material is impregnation with non-carbonaceous nanoparticles. During impregnation metal oxides such as nickel, copper, iron, zinc and mixed metals interact with the carbonaceous sample after a series of steps which include calcination and drying. In this process, it is important for the carbonaceous
surface to be hydrophilic as this will allow good penetration of the nanoparticles. The obtained material is used in various applications as it has new features like electrochemical and catalytic activities.

(v) Incorporation of polymers – To modify the surface structure of carbonaceous materials, polymers can be used to improve the performance on various applications. This method basically involve wet impregnation where often a solution containing a suitable monomer, initiator and a crosslinker is prepared and introduced on a carbonaceous sample. For methanol fuel cell application a study was investigated by coating the mesoporous carbon surface particles with polypyrrole to enhance the carbon strength. During the process, polypyrrole thickness together with the time taken for the monomer to react was controlled and the results indicated that the carbon pores remained accessible for further functionalization with Pt nanoparticles. So this point out that with the appropriate polymer coating methods, the porosity can be maintained.

2.3.3 Heavy metals removal using carbonaceous materials

There are many ways of incorporating functionality on carbonaceous material. In heavy metals removal for example oxidative treatments are mostly employed to introduce more oxygen groups on the surface to form a metal complex through adsorption process. Activated carbon is still popular on decontaminating wastewater but currently cheap precursors (like agriculture waste) are being used. Experimental studies have been conducted to study the adsorption of heavy metals (Hg, Pb and Cr ions) onto a carbonaceous surface and mainly concerning on the mechanisms involved. As carbonaceous materials get to be converted to adsorbents of varying surface area and pore structure through different treatment methods these studies indicated that the adsorption capacity is attributed to the porosity, internal surface area and surface reactivity of the material.
2.4 Coke

Coke is obtained through the processing of oil or coal by pyrolysis. Some researchers have explained that it mainly concentrates on carbon-hydrogen atoms and referred to coking process as a carbon rejection method.\textsuperscript{33-34} Coke has attracted a lot of interest in wastewater treatment research because of its ability to act as a great precursor for preparing high surface area on the production of activated carbon due to its high carbon content.\textsuperscript{35} Chlorinated organics and colours were removed from pulp mill waste water using coke derived activated carbon\textsuperscript{36} and lately raw coke without activation has shown to remove vanadium and naphthalic acids from tailing pool waters.\textsuperscript{37} There has been tremendous adsorption strength associated with petroleum coke once physically and chemically treated in aqueous solution for pollutants removal. This was linked to its macro and mesoporous range revealing low micropore volume which leads to its ability for contaminants to adsorb in a liquid phase.\textsuperscript{38} It has been used to remove heavy metals together with phenols in wastewater purification.\textsuperscript{39} Coke was also reported as a promising adsorbent in controlling trinitrotoluene hazardous red water as it was found that the acute toxicity decreased to a larger extent after treatment.\textsuperscript{40} Recently, it was proved to be a viable adsorbent to treat oil sands process affected water which was in water and retained in settling basins after contact with oil.\textsuperscript{41}

2.4.1 Formation of coke

The by-product obtained through the processing of oil into more useful products in the absence of oxygen is termed petroleum coke (pet coke). In the oil refining process, the thermal upgrading temperature (550 °C-625 °C) is set to degrade the asphaltene fractions of oil to more useful products or synthetic crude oil and the residue solid formed is termed coke.\textsuperscript{48} The material obtained by destructive distillation of coal in the absence of air inside the coking ovens is referred to as metallurgy coke (met coke).\textsuperscript{42-43}
There are three changes that occur during the transformation of coal to coke:
deromposition of coal to form plastic layers at the oven walls (at 375 °C-475 °C),
semi-coke formation after aromatic hydrocarbon compounds development (at 475 °C-600 °C) and solid coke formation (at 600 °C-1100 °C). During the coking process minerals undergo desulphurisation, decarbonation, dehydration, dehydroxylation and polymorph transformation. The amorphous phase is the major phase in coke because three polymorph forms of titanium dioxide present in coal were found to be also present after coal carbonisation.

![Fig. 2.2: Schematic diagram of the coke production process from coal](image)

Fig. 2.2: Schematic diagram of the coke production process from coal
2.4.2 Classification of coke

Coke is divided into two categories: anisotropic and isotropic. For anisotropic both the vapour and liquid derived cokes are included; these are highly ordered and show a layered macroscopic structure. The isotropic coke is from non-fluid precursors and hinders the molecules from aligning.

2.4.3 Chemical and physical properties of coke

Structurally, coke has aromatic rings bound together by ether and methyl groups with the presence of other trace elements of minerals and metals. It is a heterogeneous substance, its colour varies from grey to black and said to be insoluble in organic solvents. The pores on coke are normally filled with mineral matter. Typical example of textural features like size, shape and orientation of a certain coke plant is given in Table 2.2.

2.4.4 Applications of coke

Metallurgical coke (about 90%) is mainly used in the blast furnace operation for the production of iron. It plays three important roles: it acts as a reducing agent, as a permeable support and also as a fuel in the blast furnace operation.
largest steel producer in South Africa is Arcelor Mittal which is found in Newcastle, Vereeniging, Pretoria and Saldana. To test the quality of coke before blast furnace operation application, reactivity index (CRI) and coke strength after the reaction (CSR) are determined. Coke properties and structures depend on the initial rank of coal and how the coking process occurred.50

Environmental pollution from coal gasification which emits sulphides like hydrogen sulphide (H\textsubscript{2}S) is still a challenge in nature and there is still a need for off gas purification processes. The metal-base adsorbents have been candidates in removing this gases but were not significant enough to lower the emissions to sub ppm level.55-56 Removal of sulphides to the allowable limit was obtained when using activated coke as a dry method of cleaning the gases. This was found to be chemically stable and cheaper than metal-based sorbents.57 In addition to that, it has been reported that functionalizing activated coke with KOH and zinc impregnation would enhance the adsorption performance of H\textsubscript{2}S.57-58

Petroleum coke is a readily available material and most abundant in Canada for bitumen upgrading.59 As a result of high percentage of organic carbon on coke, it serves as a possible option for aquatic reclamation. With too much production of petroleum coke (over 2000 tons per day) in Syncrude Canada, it had to be stored because it was more than enough for combustion.38 The great concern on coke sites was if coke was not harmful to the surrounding environment. Leaching experimental tests were made to confirm this and the study concluded with regards to the amount of contaminants found in coke proved that organic substances (such as polycyclic aromatic hydrocarbons) were not detected as leachate.60 Separate field trials were investigated in natural environment (aquatic and soil) on coke impact. The conclusion of these studies was that coke is believed to be inert or does not show any negative impacts to natural environment.61-62 This inertness may be due to the fact that trace metals present in coke are strongly buried by the high carbon matrix making it to be difficult to be accessed by water.60
Table 2.2: Pet coke physico-chemical properties\textsuperscript{51-53}

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shape</td>
<td>Round spheres</td>
</tr>
<tr>
<td>Size</td>
<td>Uniform-medium to fine</td>
</tr>
<tr>
<td>Structure</td>
<td>Onion-like layers</td>
</tr>
<tr>
<td>Surface area (m(^2)/g)</td>
<td>10.7-12.2</td>
</tr>
<tr>
<td>Density (g/cm(^3))</td>
<td>1.52</td>
</tr>
</tbody>
</table>

Proximate analysis

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture</td>
<td>5.28</td>
</tr>
<tr>
<td>Ash content</td>
<td>0.31</td>
</tr>
<tr>
<td>Volatile matter</td>
<td>3.93</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>90.48</td>
</tr>
</tbody>
</table>

Ultimate analysis

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphur</td>
<td>5.32</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.83</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1.41</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>1.74</td>
</tr>
<tr>
<td>Carbon</td>
<td>82.28</td>
</tr>
</tbody>
</table>
2.5 Polymer coating

Carbonaceous materials can be converted to the desired product of choice through various treatment methods. Polymer coating is another way of modifying the surface properties of carbonaceous materials specifically for adsorption purposes where the wettability of the material can be altered. This method is practically straightforward and avoids complicated polymerization reactions. In lithium ion battery industries, the carbon surface has mostly been coated with electroactive and conductive polymers (such as polythiophene and polypyrrole) to improve the electrochemical performance. Also in the immobilization of mercury from water, the adsorption properties of activated carbon were enhanced by incorporating polysulphide rubber on the surface through polymer coating method. Introducing sulphur atoms on activated carbon improved the adsorption ability of mercury in aqueous solution as it is known that sulphur have high affinity for mercury.
2.5.1 Composite from hydrophilic polymers

For materials which are rich in carbon and hydrophobic in nature (like coke), incorporating hydrophilic polymers to enable the particles to be stable in water is necessary. The drawback associated with hydrophilic polymers attached to the carbonaceous surface is that they tend to dissolve in water with time. However, when the material is cross-linked, water molecules will be absorbed and the composite swell but does not dissolve in water. Methods such as photocrosslinking, gamma irradiations, freeze-thaw cycles and electron beam are able to crosslink the polymers. So far little attempt has been made to study the coke hydrophilic polymer composite on the removal of heavy metals in aqueous solution however a crosslinked polymer composite of chitosan have been incorporated with hydrophilic polymers PVA on recovery of cadmium ions from aqueous solutions.

2.5.1.1 Coating with poly vinyl alcohol (PVA)

Poly vinyl alcohol is desired for many purposes especially in biomedical and pharmaceutical applications due to its low toxicity and biocompatibility. On the removal of dye from wastewater PVA coated carbon black was used and it was confirmed that the dye uptake capacity was improved. In another study, glass powder particles were coated with PVA for the adsorption of borine serum and the adsorption was found to increase four times more than the uncoated particles. Coating with PVA was not only effective in aqueous solution but also in the environmental air to adsorb odorous emissions. In the livestock air treatment, activated carbon was coated with PVA for biofiltration and due to PVA (capable of absorbing moisture) the composite removed 80% of ammonia and 97% of hydrogen sulphide which improved the ability of the activated carbon to work very well.

2.5.1.2 Coating with poly ethylene glycol (PEG)

Poly ethylene glycol is a non-toxic water soluble polymer. It has been approved in biomedical applications e.g. in homoperfusion systems, where they treat drug
poisoning patients using charcoal, they experienced problems of blood cell deformation and fine particle generation and which was overcomed by coating the charcoal granules with poly ethylene glycol and they lastly crosslinked the product using gamma irradiation as this was used in an aqueous solution (blood). The adsorption capacity of the obtained product was enhanced.\textsuperscript{72}

2.5.1.3 Coating with poly vinyl pyrrolidone (PVP)

This is an organic polymer which has been used in many cases to improve adhesion of carbon fiber. Because of the carbonyl group present in poly vinyl pyrrolidone it has also been applied in adsorbing polyphenols from apple juices.\textsuperscript{73} In pharma industries it is used to prepare various drugs more especially for controlled drug release.\textsuperscript{74} In chromium removal from aqueous solution, silica gel and activated carbon have been coated with poly vinyl pyrrolidone to improve the adsorption strength.\textsuperscript{75-76}
2.6 References


Moreno-Castilla C., Carrasco-Marin F., Malodonado-Hodar F.J., Rivera-Utrilla J. Effectas of non-oxidant and oxidant acid treatments on the surface


46 Hilding T. Evolution of coke properties while descending through a blast furnace. PhD Thesis. Lulea University of Technology. 2005


CHAPTER 3
EFFECT OF ACID TREATMENT AND WET CHEMICAL OXIDATION ON THE SURFACE PROPERTIES OF COKE

3.1 Introduction

Coke is a by-product obtained through the processing and refining of oil into more useful products such as diesel oil. Due to the increase of oil refining industries and the demand of heavy oil processing coke is becoming abundant and cheap in the market.\(^1\)\(^-\)\(^3\) This form of coke is called petroleum coke. It is most likely to have nickel, vanadium and iron from crude oil refining therefore is hardly used in any production processes.\(^4\) Due to large production and high carbon content, coke became an economical motivation for wastewater treatment plants.

The other form of coke is metallurgical coke, which is produced through destructive distillation of coal inside the coke oven in the absence of oxygen.\(^5\) Metallurgical coke plays various roles in the blast furnace operation as a raw material and is also a residue or a by-product of furnace operations for the production of steel.\(^6\)\(^-\)\(^7\) Coke generally have aromatic rings bound together by ether and methyl groups.\(^8\) Moreover, the properties and structure of coke depend on the initial rank of coal and how the coking process occurred.\(^9\)

Coke is referred to be a good precursor of a well-known high surface area activated carbon as a result of its high carbon mass. Activated carbon is of great interest in terms of metal recovery in aqueous solutions by adsorption process. However, in large effluents activated carbon is not an economical option as its processing costs are high. Lately, implementations of rich carbon based materials other than activated carbon in remediation of metals in water were investigated. It has been shown that untreated coke do have some adsorption strength to heavy metals, however its capacity is low.\(^10\)\(^-\)\(^11\) This also applies to when untreated coke was used to remove napththenic acids together with total acid extractable organics from tailing water deposits.\(^12\) This may be due to the lack of initial pores on coke
surface caused by the stable micro graphitic structures (naphthalene, anthracite and pyrene) found in coke which all these encourage a need for coke modification before use. Moreover, for adsorption affinity improvement chemical treatment is essential to introduce suitable functional groups on coke surface. Coke is also made up of inorganic matters which are largely based on oxides called coke ash. The presence of these minerals reduces coke strength and said to block the carbon porosity of the material. In order to reduce mineral matter non-oxidant acids like hydrochloric and hydrofluoric acids are mainly used. Demineralization process is not only capable of removing the ash content but also alters the surface area as well as the pore texture of the carbonaceous material. Moreover, it has been investigated that in the case of heavy metal adsorption from aqueous solution, the adsorbent chemical nature determined by surface complexes have more influence than the surface area and the porosity of the adsorbent. The surface complexes are the results of acidic functional groups such as carboxyl, phenolic hydroxyl, lactone and quinone present on the surface of a material after treatment with an oxidizing agent. So far, oxidative treatments have been found to be the best way of introducing oxygen containing functional groups as this is a significant step of obtaining high performance adsorbent materials.

The study objective is therefore to assess how the surface chemistry as well as the texture of coke particles change after demineralization with HCl and further oxidized with hydrogen peroxide for addition of oxygen functional groups. For detailed understanding on the effect of wet chemical treatment, characterization in terms of surface functional groups, morphology, elemental composition, pore size distribution and lastly thermal stability were investigated.

3.2 Experimental

3.2.1 Materials

Coke sample was obtained from Macphail coal distributors in South Africa. The hydrogen peroxide used for coke oxidation and hydrochloric acid (HCl) for demineralization were procured from Merck Chemicals South Africa.
3.2.2 Preparation and modification of coke powder

The raw coke was grounded in a jaw and roll type crushers to obtain small size particle. This was then introduced to a ball mill to obtain a powdered coke. The powder was passed through a 106 µm sieve to obtain experimental samples. This was then subjected to oxidation in liquid phase using hydrogen peroxide (32% v/v) and stirred for 3 hours at 323 K. The obtained product was further treated with HCl (32%) for demineralization purpose. Finally the modified coke was rinsed under suction with distilled water and the obtained material was dried at 383 K in hot oven for overnight. The obtained coke product was denoted as F-Coke.

3.3 Characterisation techniques

Several techniques were used to characterize the raw and the modified coke powder. X-ray fluorescence (XRF) analysis was done by using Philips Magix Pro XRF spectrometer. For XRF analysis, a homogeneous glass disc was made on coke ash by fusion with lithium tetraborate. The coke was burned at 800°C for overnight to obtain the carbon free coke and the resultant ash was used for XRF analysis.

X-ray analysis of the samples was done on with X Pert Diffractometer by PANalytical. X-ray diffraction spectra was obtained by exposing samples to X-rays with 2θ angle using Cu (K) radiation with the applied voltage and current of 40 kV and 40 mA, respectively. Ash content determination was obtained by calcination of coke and acid treated coke in the muffle furnace following the ASTM D7582 method.  

For structural configuration, qualitative analysis was performed using a Fourier transformed infrared spectrometer (Perkin-Elmer Spectrum). This was carried out by using KBr disc to prepare the samples and the spectral range varied from 4000 to 400 cm⁻¹. The morphology of the material was examined using JEOL scanning electron microscope (SEM) under a 20 kV electron acceleration voltage coupled with energy dispersive (EDS) for elemental analysis. Thermal analysis of the samples was done by using Perkin-Elmer TGA 4000 analyser, where 10 mg of the
sample was taken and heated with the heating rate of 20°C min-1 in the temperature range of 30-900°C using oxygen gas.

3.4 Results and discussion

3.4.1 X-ray fluorescence (XRF)

The coke ash was analysed by XRF and the major mineral phases identified were SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, CaO and TiO\textsubscript{2}. The mineral composition of coke was summarized in Fig. 3.1. The obtained values are reliable and consistent with the oxides range mentioned by standard methods for coke and coal ash (ASTM D 4326 – 04).\textsuperscript{22} The total ash content of the parent coke obtained by incineration of coke at 900 °C was 15.04% while the one obtained after demineralization was 4.72%. About 70% of inorganic materials were removed by acid treatment.

![Fig. 3.1: Composition of mineral particle of raw coke ash (wt %) expressed as oxides](image)

3.4.2 Scanning electron microscope with energy dispersive X-ray analysis (SEM/EDS)

The chemical and physical natures of coke inorganic matter are heterogeneous therefore; coke characterization requires many techniques for better
understanding. The elemental compositions of coke before and after modification are shown in Table 3.1.

Table 3.1: Elemental compositions of raw and treated coke samples by EDS analysis (wt %)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si</th>
<th>Fe</th>
<th>Al</th>
<th>C</th>
<th>O</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-C</td>
<td>2.25</td>
<td>0.91</td>
<td>1.52</td>
<td>77.78</td>
<td>16.89</td>
<td>0.65</td>
</tr>
<tr>
<td>F-C</td>
<td>0.11</td>
<td>0.15</td>
<td>0.15</td>
<td>90.08</td>
<td>8.53</td>
<td>0.98</td>
</tr>
</tbody>
</table>

where, R-C: Raw coke, F-C: Acid treated coke.

It can be observed from EDS analysis (Table 3.1) that acid treatment removed the minerals found in raw coke. This is confirmed by a decrease in Si, Al and Fe by 83-95%. Carbon concentration increased after acid treatment as a result of non-carbon phases being removed with acid. The non-acid treated coke has more oxygen than the acid treated samples. This could be due to the fact that the oxygen in the parent coke is present as inert oxides therefore, during acidification it was removed in the form of minerals and the remaining oxygen resulted from the hydrogen peroxide treatment.

SEM visual examination (Fig. 3.2) of the parent and modified coke samples do not show significant changes. However, it is recognized on the images that the raw coke is somehow compact and graphitized indicating minimal activation points. After acid treatment the voids show up clearly, and the coke structure is loosened up as a result of many pores occurring.
3.4.3 X-ray diffraction (XRD) studies

The amorphous and crystalline natures of coke were identified using X-ray diffraction analysis. The distribution of mineral was difficult to be observed on coke as it contains high carbon percentage which produces high intensity which reduced the amount of minerals present. However, small peaks at around 45° and 50° which can be attributed to aluminium silicon oxide (mullite) and silicon oxide (quartz) are observed in the spectrums of raw coke as well as the acid treated coke (Fig. 3.3). The XRD patterns obtained followed the same trend indicating that the coke crystal structure was not significantly altered during modification process. However, the acid treated coke showed broader peaks than raw coke which could imply the disorder formation during the modification process. The diffraction peak at 2θ = 26° corresponds to graphite which appears as the intense peak in carbonaceous materials.23
3.4.4 FT-IR spectroscopy

Functional group measurements of raw and acid treated coke samples were obtained by using FT-IR spectroscopy (Figs. 4.4). This was to explore the functional group change brought by modification. In case of FT-IR spectra of raw coke (Fig. 4.4a), the major peaks are obtained at around 3400 cm$^{-1}$ (-OH stretching), 1600 cm$^{-1}$ (C=C stretching), 1400cm$^{-1}$ (C-H stretching) and 1100 cm$^{-1}$ (C-O stretching). However, in the FT-IR spectrum of acid treated coke, the intensity of the peak at 1400cm$^{-1}$ (observed in the spectrum of raw coke) was found to decrease (Fig. 4.4b). This may be due to the reactivity of C-H groups being oxidized leading to the noticeable and intense peak at 1100 cm$^{-1}$ indicating the presence of C-O and C-O-C groups$^{24}$ and the appearance of a weak band at 1780 cm$^{-1}$ (Fig. 4.4b) is attributed to stretching vibrations of carboxyl groups.$^{21}$
Chapter 3: Effect of acid treatment and wet chemical oxidation on the surface properties of coke

3.4.5 Thermogravimetric analysis (TGA)

Weight change in a material with temperature can be determined by thermogravimetric analysis which is an alternative way for performing proximate analysis. The acid treated coke shows the highest percentage mass loss with the least residue of about 4% which correspond to its ash content obtained in the study using ASTM standard method. A closer look at a region between 460 °C to 630 °C, indicates that acid treated coke seems to degrade later than the raw coke. This can be as a result of incorporation of carboxylic groups which increase the thermal stability of the material. The insignificant weight loss at 100 °C to 200 °C is attributed to moisture content. From Fig. 3.5 it is worth noticing that raw coke degraded faster and the residue was greater than the functionalized coke due to mineral matter still present on the raw coke sample.

Fig. 3.4: FT-IR spectra of: (a) raw coke and (b) acid treated coke
Chapter 3: Effect of acid treatment and wet chemical oxidation on the surface properties of coke

3.5 Conclusion

The study demonstrated the influence of coke modification with HCl and treatment with an oxidizing agent hydrogen peroxide. FT-IR spectroscopy revealed the introduction of additional acidic functional groups while, the decrease of mineral matter through acid treatment was revealed by SEM micrographs showing a loose structure and pore enhancement. Thermal behaviour indicated low percentage residue on the modified coke compared to the raw coke sample, supporting the demineralization process. The modified material degraded later than the raw coke as the results of newly formed functional groups. Coke characterization suggests the effectiveness of this method because of the increase in concentration of anchoring sites which act as adsorption positions for metal ions.
Chapter 3: Effect of acid treatment and wet chemical oxidation on the surface properties of coke

3.6 References


CHAPTER 4
INFLUENCE OF INCORPORATING HYDROPHILIC POLYMERS ON COKE SURFACE PARTICLES

4.1 Introduction

Material which is made by combining two or more components is called a composite. These components tend to stick together to maintain each other's interface and act together to give a much improved concert. They should not dissolve in one another nor completely merge. However, the separate components retain their characteristics while acting together to give the required mechanical strength, stiffness or any other factor of interest to the composite fragment unlike when doing blending. Metallurgical coke for instance is used in the blast furnace operations where it is used as a reducing agent for iron production. To be effective enough its strength and reactivity should be controlled through.¹ Since with the coal blending only the strength of coke was enhanced and the reactivity weakened, coke composite was prepared by coating coke particles with polyvinyl alcohol and the resulting composite was proved to have both improved strength and reactivity.² Polymer composites have versatile applications especially in today's adsorption technology.

Recently, coating or grafting materials with hydrophilic polymers like polyvinyl alcohol, polyethylene glycol and polyvinyl pyrrolidone to stabilize the resulting composite in water is of great interest. Common materials used as support for composite adsorbents include activated carbon³, carbon black⁴, glass powder⁵, chitosan⁶ and alginate⁷ all these were used for the removal of pollutants from wastewater. One major concern with hydrophilic polymers in large quantities of water is that they erode or dissolve in water and may be loosely attached to the support material particles with time. However, when the material is cross-linked, water molecules will be absorbed and the composite swells but does not dissolve in water. Therefore, the durability of the resulting composite is vital especially
when working with aqueous solutions. Crosslinks prevent polymer chains from moving around when chains become hydrated. One way of crosslinking is to introduce initiators such as potassium persulphate in the reaction which then decompose to form free radicals as indicated in scheme 1 below.

Scheme 4.1: Reaction mechanism of polyvinyl alcohol with potassium persulphate

Potassium persulphate reaction leads to generation of $SO_4^{2-}$ free radicals which react to form tertiary radicals on a polymer chain and the insolubility of polymer composite is due to the reaction between the two macro radicals in the crosslinking step.

Hence, this work was carried out to study the changes in the modified and unmodified coke powder after being introduced into the hydrophilic polymer solutions and immobilized using potassium persulphate as a crosslinking initiator.
In order to evaluate structural transformation atomic ordering, morphology, surface area, pore volume and thermal stability were investigated.

4.2 Experimental

4.2.1 Materials

Hydrophilic polymers i.e. PVA, PEG and PVP used for coating purpose were purchased from Sigma Aldrich and used as received. Potassium persulphate was procured from Merck.

4.2.2 Polymer coating

For coating purposes 5% (w/v) aqueous solution of PVA, PEG and PVP was prepared and kept in contact with modified and raw coke powder for 12 h. This was achieved by following the schematically outlined procedure in Fig.1. A known amount of coke was added into a polymer solution. The obtained dispersion was kept overnight in order to give the polymer chains enough time to adsorb onto the coke particles surface.

It has been noted that the hydrophilic polymer shells on carbonaceous materials erode in the large amount of water due to the inclination of these polymers on stretching back to water. In order to immobilize the polymer composite, crosslinking reaction was induced by adding 1.25% (m/v) potassium persulphate solution to the above dispersion and stirred for 1 hour at 50 °C in a nitrogen atmosphere.
4.3 Characterization techniques

The specific surface area and pore volume of raw coke together with the polymer coated coke were measured by sorption of nitrogen at -196 °C on a Brunauer-Emmett-Teller (BET) Sorptometer. The morphology was examined using JEOL scanning electron microscope (SEM) under a 20 kV electron acceleration voltage. Raman spectra were measured using RamanMicro 200 Microscope where coke samples were placed on a glass slide in a powder form without any solvent. The thermal stability of the samples was carried out by using Perkin-Elmer TGA 4000 analyzer, where 10 mg of the sample was taken and heated with the heating rate of 20 °C min^{-1} in the temperature range of 30-900 °C using oxygen gas.
4.4 Results and discussions

4.4.1 Brunauer-Emmett-Teller (BET)

The measured BET surface area of raw coke was 1.058 (m²/g) and upon treated with acid it went up by 8% to 1.152 (m²/g), which indicate the successful removal of minerals present in the raw coke. Coating with polymer films decreased the surface area as well as the pore volume of the material as shown in Table 4.1. This is attributed to polymers depositing to coke surface particles and filling up the small cavities that were present in coke.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-C</td>
<td>1.058</td>
<td>0.0458</td>
</tr>
<tr>
<td>F-C</td>
<td>1.152</td>
<td>0.0507</td>
</tr>
<tr>
<td>R-PVA</td>
<td>0.120</td>
<td>0.0139</td>
</tr>
<tr>
<td>F-PVA</td>
<td>0.193</td>
<td>0.0221</td>
</tr>
<tr>
<td>F-PEG</td>
<td>0.158</td>
<td>0.0189</td>
</tr>
<tr>
<td>R-PVP</td>
<td>0.083</td>
<td>0.0137</td>
</tr>
<tr>
<td>F-PVP</td>
<td>0.194</td>
<td>0.0133</td>
</tr>
</tbody>
</table>

where, R-C: Raw coke, F-C: Acid treated coke, R-PVA: PVA coated raw coke, F-PVA: PVA coated acid treated coke, R-PEG: PEG coated raw coke, F-PEG: PEG coated raw coke, R-PVP: PVP coated raw coke and F-PVP: PVP coated acid treated coke

4.4.2 Scanning electron microscope

In order to determine the morphological changes due to the presence of polymers on coke particles SEM analysis was carried out. The scanning electron
micrographs (SEMs) in Fig. 4.2 (a-d) showed that the coke particles were actually coated with polymers. Here it indicates that the uncoated coke particles are likely to be rough, heterogeneous and have voids throughout, whereas on the other hand the coated particles are smooth and pores are slightly blocked. These findings accord the coating of coke particles with polymer films.

Figs. 4.2: SEM micrographs of (a-b) uncoated raw coke and (c-d) is PVP coated acid treated coke samples
4.4.3 Raman spectroscopy

Conjugated carbon double bonds lead to high Raman intensity, therefore Raman serves as a best tool to study the atomic ordering of a material. For carbonaceous materials, two predominant peaks appear on the spectra. Those are: D-band/peak which is likely visible at around (1355 cm\(^{-1}\)) and G-band at (1580 cm\(^{-1}\))\(^{10-11}\). Higher disorder (D-band) is a result of six fold rings whereas the gravitic nature (G-band) is associated with the in plane stretching bonds of sp\(^2\) carbon atoms as shown in Fig. 4.3. The positions of the D-band and G-band are given in Table 4.2 with their corresponding intensity ratios. From the results, it is observed that coke is amorphous or disordered. This is supported by the higher D-band in Fig.4.4 which is the distribution of vibrational modes that are amorphous in nature. Previously, the difference between amorphous and graphitic was based on the note that graphite could be converted to gravitic acid by using oxidizing agents whereas the amorphous carbon was known not to be affected in this regard.\(^{12}\) However, the structure of amorphous materials can be destructed by heating.\(^{11}\) So from the obtained results it was observed that the atomic ordering of coke technically remained the same as there are insignificant changes upon acid treatment and polymer coating. Intensity ratio (I_D/I_G) approaching zero suggests an increase in graphitic mode which is contrary to the obtained results as the structure was amorphous.

---

**Fig. 4.3 Raman vibration modes**\(^{11}\)

---
Chapter 4: Influence of incorporating hydrophilic polymers on coke surface particles

Fig. 4.4: Raman spectra of raw coke

Table 4.2: Raman peak positions and intensity ratios ($I_D/I_G$)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>D-band (cm$^{-1}$)</th>
<th>D-band (cm$^{-1}$)</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-C</td>
<td>1344</td>
<td>1590</td>
<td>1.038</td>
</tr>
<tr>
<td>F-C</td>
<td>1350</td>
<td>1600</td>
<td>1.024</td>
</tr>
<tr>
<td>F-PVA</td>
<td>1344</td>
<td>1596</td>
<td>1.046</td>
</tr>
<tr>
<td>F-PEG</td>
<td>1350</td>
<td>1600</td>
<td>1.021</td>
</tr>
<tr>
<td>F-PVP</td>
<td>1346</td>
<td>1602</td>
<td>1.053</td>
</tr>
</tbody>
</table>
4.4.4 Thermogravimetric analysis (TGA)

![Thermographic curve of raw coke, acid treated coke and polymer coated coke](image)

**Fig. 4.5:** Thermographic curve of raw coke, acid treated coke and polymer coated coke

**Table 4.3: Decomposition of coke and its composite with temperature**

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Percentage decomposition at different temperatures (°C)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IDT</td>
<td>5%</td>
</tr>
<tr>
<td>R-C</td>
<td>243</td>
<td>469</td>
</tr>
<tr>
<td>F-C</td>
<td>347</td>
<td>548</td>
</tr>
<tr>
<td>F-PVA</td>
<td>277</td>
<td>488</td>
</tr>
<tr>
<td>F-PEG</td>
<td>178</td>
<td>441</td>
</tr>
<tr>
<td>F-PVP</td>
<td>135</td>
<td>488</td>
</tr>
</tbody>
</table>

Where, IDT: initial decomposition temperature, FDT: final decomposition temperature and Res: residue
TGA measurements showed a high mass loss of ca. 87% for raw coke and ca. 91% for PVA coated, PEG coated and PEG coated functionalized coke sample. This indicates the improvement of thermal stability upon merging with the polymers. For acid treated coke sample the highest loss was (ca. 96%) at a region between 600 °C and 870 °C.

From Fig. 4.5 it is noticed that raw coke degraded faster and the residue was slightly greater than the functionalized and the polymer coated coke. Fig. 4.6 shows the thermogravimetric patterns of the pure polymers (PVA, PEG and PVP) at high temperatures. The two thermogravimetric curves (Figs. 4.5 and 4.6) demonstrate that mass loss rate of polymers decrease with the incorporation of coke particles, therefore suggesting that coke content significantly improves the stability of polymers. Moreover, the final decomposition temperature (FDT) of the acid treated coke as well as polymer coated coke samples was found to be higher than that of the raw coke. This confirmed that the thermal stability of the coke increased after coating with different polymers.

Fig. 4.6: Thermogravimetric analysis of pure PVA, PEG and PVP samples
4.5 Conclusion

In this study it was indicated that fusing the coke particles with hydrophilic polymers lowered the surface area as well as the pore volume of the material. This was also supported by the morphological changes obtained from SEM analysis, where the accessible voids that were present before treatment were visible and were somehow blocked after coating with polymer films. There were no significant changes obtained on atomic ordering measured by Raman spectroscopy. Thermal stability was improved on the polymer composite in comparison with the parent coke, however the parent coke was found to have the least percentage residue as compared to the composites and acid treated coke samples.
4.6 References


5.1 Introduction

Heavy metals have strength not to disappear, rather they move around the environment over great distances through air and water streams. These metals are soluble in water and resulting water bodies to become the major sites of heavy metals deposits. Industrial power plants such as electroplating, mining and smelting operations consume large volumes of process water polluted with heavy metals. Till today, it is still an on-going objective for environmentalists to innovate better procedures to replenish wastewater in an economical manner since it is still a challenge for industries to release large effluents of contaminated water on a daily basis. The implications of adsorption technologies seem to bring solutions to water decontamination issues because of its wide applicability.

It is well known that activated carbon is of great interest in terms of metal recovery in aqueous solutions by adsorption process. In many low cost adsorbents that have been used, coke has been found to be a promising adsorbent in contaminated water control although its adsorption capacity is very low. In most cases coke is used to prepare activated carbon due to its low ash content and the fact that it is already carbonised. Activated carbon has high affinity for metal ions in aqueous solution. In spite of the efficacy of activated carbon in metal recovery, it is not an economical option for large effluents as its processing costs are high. Therefore, there is still a need to investigate the effective adsorbents which require cheap and simple preparation processes that avoid activation using high energy. Petroleum coke is a readily available material and most abundant in Canada for bitumen upgrading. Surface modification of coke inner pores may possibly be a promising way for the immobilization of heavy metals in aqueous solution.
Hence this study deals with the uptake of lead and chromium ions from aqueous solutions by adsorption process using raw coke, acid treated coke and coke hydrophilic polymer composite. Based on the instability of coke particles due to its hydrophobic nature in water, they were fused together with hydrophilic polymers. It is crucial for the resulting composite to be durable in this study. In particular, focal areas of the present work were to investigate the properties of raw and functionalized coke based composites and its application towards adsorption properties.

5.2 Experimental

5.2.1 Instruments and apparatus

Lead and chromium ions in aqueous solutions were determined by Flame Atomic Absorption Spectrometer (AAnalyst 400 Perkin Elmer). The wavelengths selected were 283.3 nm for lead and 425.4 nm for chromium. The pH meter (Mettler Toledo) was used for pH adjustments.

5.2.2 Reagents and standard solutions

Hydrochloric acid (32%), sodium hydroxide, lead nitrate and chromium nitrate were procured from Merck Chemicals in South Africa. The stock standard solutions of Pb(II) and Cr(III) were prepared by dissolving Pb(NO$_3$)$_2$ and Cr(NO$_3$)$_3$ in de-ionized water. Working standard solutions were prepared by diluting the stock solution with de-ionized water to obtain the required concentrations.

5.2.3 Adsorption experiments

Batch experiments were carried out using conical flasks of 100.0 mL capacity. The effect of medium pH, contact time and initial concentration were conducted on Pb(II) and Cr(III). The effect of pH on adsorption was investigated at pH range between 2.0 and 9.0 using either 0.1 M HCl or 0.1 M NaOH to adjust the pH at room temperature. For kinetic studies, 500 mg of the adsorbent was shaken with 200.0 mL of Pb(II) (25 ppm) and the filtered solution was taken at different time
intervals. The contents were constantly agitated in a mechanical shaker at 160 rpm. Adsorption isotherm measurements were performed by agitating 50 mg of the adsorbent with 20.0 mL of varying metal concentrations from 2.0 to 70.0 ppm at an optimal pH of 6.0. At the end, the adsorbent was filtered out and concentration in the supernatant was determined using flame Atomic Absorption Spectrometer (FAAS). The amount adsorbed was therefore determined from the difference in initial and residual concentration in the liquid phase using the formula:

\[ q_e = \frac{(C_i - C_e)V}{m} \]  \hspace{1cm} (5.1)

Where: \( C_i \) (mg/L) is the initial concentration of Pb(II), \( C_e \) (mg/L) is the concentration at equilibrium, \( V \) (L) is the volume of the solution and \( m \) (g) is the mass of the adsorbent.

5.2.4 Limit of detection

This is the lowest concentration that can be measured by the instrument. It was calculated based on three times the standard deviation of blank solution tested in eight runs. For quality control purposes ie. reproducibility, precision and reliability, the data was recorded in triplicate and only the average values were reported.

5.3 Results and Discussion

5.3.1 Effect of pH

The degree of metal adsorption is technically related to the pH of the aqueous solution due to dissociation of adsorbent active sites as well as the speciation of metal ions in aqueous phase which are affected by solution pH.\(^8\) Fig. 5.1 shows that the uptake of metals ions on coke and coke based composites depend on the solution pH. Hence the effect of hydrogen ion concentration in the study was examined at pH ranging from 2 to 9 as indicated in Fig. 5.1. Here it shows the results of Pb(II) and Cr(III) uptake at various pH values of which the same trend was followed for coke and its composites. Initially or at low pH values there is poor
metal adsorption as a result of excess amount of hydronium ions (H$_3$O$^+$) compared to the metal ions present in the solution. Therefore the H$_3$O$^+$ take over on the adsorbent binding sites led to metal ion being free in the solution.

Fig. 5.1: Effect of pH on (a) 25 mg/L solution of Pb (II) and (b) 25 mg/L solution of Cr(III), agitation speed = 160 rpm, temperature ± 25°C, contact time 120 min and adsorbent dosage = 0.05 g/20 mL
Increase in metal ions uptake is observed from pH 2 up to 6. This may be explained by the fact that increasing the pH of Pb (II) in solution results in various species being noticeably present. For example at pH 6, Pb(OH)$^{+}$ and Pb$^{2+}$ are the major ions in the solution, making it easier to be accessed or to interact with surface functional groups present in the adsorbent and once again in increasing the pH to higher values than 6, there is a formation of metal precipitation and the adsorbent weakened again. This drastic deterioration was due to the change of species to a negatively charged ion Pb(OH)$^{3-}$ which was now resisting on the surface active sites of the adsorbent.

In the case of Cr(III) removal, the adsorbent materials were effective until the pH of 7 was achieved unlike in Pb(II) where pH 6 was the optimum value. One of the main reasons is the presence CrOH$^{2+}$ species which forms at around pH 5 and strongly forms a complex with the adsorbents. So once increasing the solution pH to 7, Cr(III) begins to appear in the form of a neutral and a monovalent state of Cr(OH)$_{3}$ and Cr(OH)$_{2}^{+}$ which still have the affinity to bind on the adsorbents surface due to positively charged ions that are still present. Decrease in metal ion adsorption at pH 9 where the neutral ions are present (CrOH)$_{3}$ is attributed to the weak interaction between the existing ion and the adsorbents surface.

5.3.2 Effect of contact time

Time effect was conducted in order to measure the time taken to reach equilibrium. The presented plots in Fig. 5.2 reveal that the removal was substantial during the first 60 min for Pb(II) and 120 min for Cr(III) thereafter insignificant changes were observed. This is probably associated with the availability of surface active sites at an earlier stage whereas with time it became exhausted leaving only the interior part of adsorbent for the uptake of metal ion which is much slower. A close look at Fig. 5.2 indicates that polymer composites were somehow slower than the coke and the acid treated coke. This delay may be due to different characteristics of the adsorbent such as degree or percentage amount of polymer coated which may require longer period for mass transfer of the metal ions.
Fig. 5.2: Effect of contact time on (a) 25 mg/L solution of Pb (II) and (b) 25 mg/L solution of Cr(III), agitation speed = 160 rpm, temperature ± 25°C, pH=6 and adsorbent dosage = 0.5 g/200 mL
5.3.3 Effect of initial metal concentration

![Graph showing the effect of initial metal concentration on Pb(II) and Cr(III) adsorption.](image)

Fig. 5.3: Effect of initial concentration for 120 min. on (a) Pb (II) solution and (b) Cr(III) solution, agitation speed = 160 rpm, temperature ± 25°C, pH=6 and adsorbent dosage = 0.05 g/20 mL
Various metal concentrations were measured to study the driving force of mass transfer between the solution and solid phases. The observations reveal that, the amount of metal ion adsorbed increased with increase in the concentration of Pb(II) and Cr(III) from 2 ppm to 70 ppm as shown in Fig. 5.3. This indicates that the adsorption process on different coke materials was dependent on the amount of Pb(II) ion and Cr(III) present in the solution.

5.3.4 Adsorption kinetics

The evaluation of adsorption kinetics in wastewater treatment is vital as it provides clear trails on reaction pathways and sorption reaction mechanisms as it explains the solid uptake rate as well as controlling the adsorbent resident time on a solid-solution interface.\textsuperscript{11} Therefore, having an idea of the pollutant rate removal makes it possible to create an appropriate adsorption treatment plant. Here two models are being proposed at to investigate the sorption mechanism that is pseudo-first order equation (based on solid capacity) and pseudo-second order (based on solid phase), respectively.\textsuperscript{11} The integrated equations employed are shown in (5.2) and (5.3):

\begin{equation}
\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t
\end{equation}

\begin{equation}
\frac{t}{q_t} = \frac{1}{k_2 q^2} + \frac{1}{q_e t}
\end{equation}

where, $q_e$ and $q_t$ are adsorbed amount in mg/g at equilibrium and at time t, $k_1$ and $k_2$ are pseudo first and second order adsorption models measured in min\textsuperscript{-1}.

Using the data summarized in Tables 5.1 and 5.2, the study shows the second order model since in first order the calculated $q_e$ does not correlate with experimental $q_e$. Therefore, first order is not favoured in the system. This means that the adsorption process is associated with two sites possession. One great benefit of the second order model is that the equilibrium capacity can be obtained directly from the measurements.\textsuperscript{12}
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![Graph showing pseudo first order kinetic plots for Pb(II) and Cr(III)]

**Fig. 5.4**: Pseudo first order kinetic plot for Pb(II)

**Fig. 5.5**: Pseudo first order kinetic plot for Cr(III)
Chapter 5: Removal of lead and chromium ions from aqueous media by raw coke, acid treated coke and coke polymer composites

Fig. 5.6: Pseudo second order kinetic plot for Pb(II)

Fig. 5.7 Pseudo second order kinetic plot for Cr(III)
Table 5.1: Lagergren kinetic parameters for Pb(II)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(q_e) (exp.) (mg/g)</th>
<th>1st order kinetic model</th>
<th>Second order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_1) (L/min)</td>
<td>(q_e) (cal.) (mg/g)</td>
</tr>
<tr>
<td>Raw coke</td>
<td>3.2374</td>
<td>0.0183</td>
<td>0.2274</td>
</tr>
<tr>
<td>Acid treated coke</td>
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<td>0.0099</td>
<td>0.1667</td>
</tr>
<tr>
<td>PVA coated coke</td>
<td>7.6948</td>
<td>0.0214</td>
<td>0.5239</td>
</tr>
<tr>
<td>PEG coated coke</td>
<td>8.2680</td>
<td>0.0101</td>
<td>0.2499</td>
</tr>
<tr>
<td>PVP coated coke</td>
<td>8.1272</td>
<td>0.0101</td>
<td>0.3280</td>
</tr>
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</table>

Table 5.2: Lagergren kinetic parameters for Cr(III)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>(q_e) (exp.) (mg/g)</th>
<th>1st order kinetic model</th>
<th>Second order kinetic model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(k_1) (L/min)</td>
<td>(q_e) (cal.) (mg/g)</td>
</tr>
<tr>
<td>Raw coke</td>
<td>2.3500</td>
<td>0.0348</td>
<td>1.5603</td>
</tr>
<tr>
<td>Acid treated coke</td>
<td>3.0165</td>
<td>0.0108</td>
<td>1.0595</td>
</tr>
<tr>
<td>PVA coated coke</td>
<td>8.6848</td>
<td>0.0233</td>
<td>7.7428</td>
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<tr>
<td>PEG coated coke</td>
<td>10.9044</td>
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<td>14.0508</td>
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<td>PVP coated coke</td>
<td>10.2872</td>
<td>0.0272</td>
<td>10.6439</td>
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</table>

The plots of \(\log(q_e - q_t)\) vs time indicated in Fig. 5.4-5.5 show deviation from the linear relationship. From the slopes and the intercepts the \(k_1\) (first order rate constant) and \(q_e\) (equilibrium capacity) were calculated. The calculated values from the plots are lower than the experimental values. Considering the \(t/q_t\) plots (Fig. 5.6-5.7), there is a superior linear relationship in coke and its composites. Furthermore, the experimental \(q_e\) values agreed with the theoretical \(q_e\) values calculated from the pseudo second order kinetic model.
5.3.5 Adsorption isotherms

The other important physiochemical characteristic for adsorption assessment other than kinetics is the equilibrium of adsorption. Equilibrium is capable of revealing the capacity of the adsorbent. Adsorbates concentrations for the effect of initial metal concentration (Fig 5.3) were used to determine the adsorption equilibrium data. The relationship between the equilibrium and the adsorbent is well described by the implication of isotherms. The two isotherms employed in this study are: Langmuir and Freundlich isotherms as expressed in equations (5.4) and (5.5).

\[
\frac{1}{q_e} = \frac{1}{K_L C_e} + \frac{1}{q_{\text{max}}} \quad (5.4)
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5.5)
\]

where: \( q_e \) is the amount adsorbed at equilibrium (mg/g), \( q_{\text{max}} \) maximum adsorption capacity of the adsorbent (mg/g), \( C_e \) is the equilibrium concentration of pollutant (mg/L), \( K_L \) is the Langmuir constant. \( K_F \) and \( n \) are the parameters of Freundlich related to adsorption capacity constants.

The applicability of the Langmuir isotherm is indicated in the plot of 1/\( C_e \) vs 1/q\(_e\) (Figs. 5.8-5.10) which give the straight line for both metal ions. Same goes for the plot of log \( C_e \) vs log q\(_e\) (Fig. 5.11-5.13) which represent the Freundlich adsorption isotherm. The two models are strictly based on assumptions. Langmuir is supported by the finite number of identical sites on a solid surface forming a mono layer whilst Freundlich assumes that a heterogeneous surface where the binding sites are not equivalent. Least squares method was used to determine the equilibrium parameter values given in Table 5.3 and 5.4. In order to determine which of the two methods is obeyed; better correlation coefficient (R\(^2\)) of each equation was used.
Fig. 5.8 Plot of Langmuir adsorption isotherm on raw coke, acid treated coke for Pb(II).

Fig. 5.9 Plot of Langmuir adsorption isotherm on PEG coated coke and PVP coated coke for Pb(II).
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**Fig. 5.10** Plot of Langmuir adsorption isotherm on raw coke, acid treated coke, PVA coated coke, PEG coated coke and PVP coated coke for Cr(III).

**Fig. 5.11** Plot of Freundlich adsorption isotherm on raw coke, acid treated coke and PVA coated coke for Pb(II).
Chapter 5: Removal of lead and chromium ions from aqueous media by raw coke, acid treated coke and coke polymer composites

Fig. 5.12 Plot of Freundlich adsorption isotherm on PEG coated coke and PVP coated coke for Pb(II).

Fig. 5.13 Plot of Freundlich adsorption isotherm on raw coke, acid treated coke, PVA coated coke, PEG coated coke and PVP coated coke for Cr(III).
Chapter 5: Removal of lead and chromium ions from aqueous media by raw coke, acid treated coke and coke polymer composites

### Table 5.3: Parameters of Langmuir and Freundlich adsorption isotherm models for Pb(II)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Langmuir</th>
<th>Freundlich</th>
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<tr>
<td></td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Raw coke</td>
<td>2.4091</td>
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<td>0.9939</td>
</tr>
<tr>
<td>Acid treated coke</td>
<td>2.9455</td>
<td>0.0340</td>
<td>0.9752</td>
</tr>
<tr>
<td>PVA coated coke</td>
<td>8.3195</td>
<td>0.1011</td>
<td>0.8691</td>
</tr>
<tr>
<td>PEG coated coke</td>
<td>9.6993</td>
<td>0.8563</td>
<td>0.9923</td>
</tr>
<tr>
<td>PVP coated coke</td>
<td>9.8425</td>
<td>0.8167</td>
<td>0.9946</td>
</tr>
</tbody>
</table>

### Table 5.4 Parameters of Langmuir and Freundlich adsorption isotherm models for Cr(III)

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Langmuir</th>
<th>Freundlich</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>Raw coke</td>
<td>9.4787</td>
<td>0.0253</td>
<td>0.9989</td>
</tr>
<tr>
<td>Acid treated coke</td>
<td>9.9404</td>
<td>0.0317</td>
<td>0.9984</td>
</tr>
<tr>
<td>PVA coated coke</td>
<td>35.8423</td>
<td>0.0155</td>
<td>0.9988</td>
</tr>
<tr>
<td>PEG coated coke</td>
<td>32.7869</td>
<td>0.0234</td>
<td>0.9953</td>
</tr>
<tr>
<td>PVP coated coke</td>
<td>34.1297</td>
<td>0.0287</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

The overall obtained adsorption isotherm data (Table 5.3) fitted both the Langmuir and Freundlich isotherm models as typical linearized graphical representations are shown in Fig. 5.8 to 5.13, respectively. This is supported by the correlation coefficient ($R^2$) of > 0.9. However comparing the two models, Langmuir equation fitted the experimental data even better for both Pb(II) and Cr(III) in the studied concentration ranges. Parameters such as $q_{\text{max}}$ (in Langmuir) and $n$ (in Freundlich) which are connected to adsorption capacity increased upon coke modification, from the demineralized coke as well as on coke fused with hydrophilic polymers. Furthermore the reported $q_{\text{max}}$ for both metal ions prove that Cr(III) was removed better than Pb(II) for all adsorbents used.
5.3.6 The detection limit and experimental precision

Following the procedure on the International Union of Pure and Applied Chemistry, detection limit is the product of three times the standard deviation of data obtained from eight runs of the blank solution. The detection limit was found to be 0.183 mg/L and the relative standard deviation was 2.67% revealing the precision of results on Pb(II) analysis and 0.329 mg/L and relative standard deviation of 4.63% for Cr(III).

5.4 Conclusion

The results of this study show that coke polymer composite demonstrated high sorption affinity towards Pb(II) and Cr(III) when compared to the parent coke. The study was found to be of first order reaction due to the kinetic data obtained and adsorption mechanism is most likely to be a chemisorption reaction. Langmuir isotherm gave a better fit from the Freundlich isotherm in equilibrium description of both Pb(II) and Cr(III) based on the linearized correlation coefficient.
5.5 References


Chapter 5: Removal of lead and chromium ions from aqueous media by raw coke, acid treated coke and coke polymer composites


6.1 Introduction

Implications of aluminum oxide, silica gel, zeolites and clay minerals, for the uptake of heavy metals in aqueous solution by adsorption technique is widely used. These materials provide high capacity of ion exchange leading to their advantage to interact with different heavy metals. In the investigation that was done to study the effect of minerals/ash present in activated carbon made from coal and charcoal for the removal of lead ions from wastewater, major minerals that were present in each carbonaceous material were identified to understand the adsorption mechanism are given in Table 6.1.

Table 6.1: Percentage mineral present in charcoal and activated carbon ash

<table>
<thead>
<tr>
<th>Mineral composition</th>
<th>charcoal ash (%)</th>
<th>activated carbon ash (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.8</td>
<td>2.8</td>
</tr>
<tr>
<td>Mg</td>
<td>3.9</td>
<td>0.1</td>
</tr>
<tr>
<td>Al</td>
<td>0.1</td>
<td>21.1</td>
</tr>
<tr>
<td>Si</td>
<td>0.4</td>
<td>20.3</td>
</tr>
<tr>
<td>K</td>
<td>1.2</td>
<td>5.6</td>
</tr>
<tr>
<td>Ca</td>
<td>40.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Mn</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>0.87</td>
<td>3.4</td>
</tr>
</tbody>
</table>

From this table, it can be observed that major minerals present in charcoal were Ca, Mg and Mn whereas in activated carbon major minerals present were Si and Al. At a given concentration activated carbon ash failed to remove the Pb ions from the solution whereas charcoal ash proved to have high affinity for Pb ions. It
was concluded that the presence of Mg and Mn are effective in binding with Pb ions unlike in the case of activated carbon. This study supports the findings of Dong et al\(^6\) who opined that Pb adsorption was not dominant on Al oxide but significantly occurs in Mn oxide. However, these findings are confusing when referring to another work investigated by Lopez-Delgado et al\(^7\) who compared coke with the blast furnace sludge and targeted the same heavy metal lead. They concluded that the perfect removal of lead ions was due to hematite/ Fe\(_2\)O\(_3\) found in the blast furnace which form bonds through hydroxyl bridges in the solution.\(^7\) The very same hematite present in the first study mentioned (Table 6.1) seemingly failed to remove the lead ions.

Many approaches have been used to characterize the properties of coke which include coke mineralogy and carbon atom structure.\(^8-9\) Coke understanding of mineral matter is largely based on oxides of the coke ash. This work attempts to characterize the coke ash and further evaluate its use for Pb (II) and Cr (III) removal in water.

6.2 Experimental

The sample of raw coke and the modified coke (treated with HCl and H\(_2\)O\(_2\)) were calcined in air for overnight using a muffle furnace at 800°C to obtain a carbon free coke. The ashes together with the parent and acid treated coke samples were used as adsorbents in the experiments. The composition of the minerals were determined by XRF and EDS as described in chapter 3 (Fig 3.1 and Table 3.1). To determine the organic matter content, loss on ignition (LOI) analysis was done on both samples of raw and acid treated coke. For the examination of physical nature of coke and its minerals SEM was used at the accelerating voltage of 20 kV.

Adsorption experiments were carried out at room temperature (22°C-25°C), for 25 mg/L concentration of Pb(II) and Cr(III) agitation speed 160 rpm for 120 min with the adsorbent dosage of 0.05g/20mL.
6.3 Results and discussion

Elemental compositions indicate that coke consists mostly of silica, alumina and iron (Fig 3.1). The inorganic matter determined based on bulk ash analysis was 15.04% and 4.72% for the parent coke and acid modified coke.

Figs. 6.1: SEM images of (a) raw coke; (b) acid treated; (c) raw coke ash and (d) acid treated coke ash
According to S Gupta et al. illustrations of SEM images, bright spots, grey colour and dark segments indicate minerals, carbon medium and pores, respectively. The examination of coke images in Figs. 3.1a-b indicates that coke minerals are in close contact with the carbon matrix or totally buried on carbon that they are not visible. Figs 3.1c-d shows the coke minerals after ashing. The coke ash images show that the minerals in coke varied considerably in shape and size. It is observed that mineral particles on parent coke ash are irregularly distributed and tend to be polygonal. The acid treated ash coke minerals have round morphology, which reflects the alteration of coke after acid treatment.

Table 6.2: Properties of coke based materials and their adsorption capacity on lead and chromium ions

<table>
<thead>
<tr>
<th></th>
<th>Pb(II) Adsorbed (mg/g)</th>
<th>Cr(III) Adsorbed (mg/g)</th>
<th>Ash content (%)</th>
<th>Loss on ignition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw coke</td>
<td>3.3669</td>
<td>4.5150</td>
<td>15.04</td>
<td>86.16</td>
</tr>
<tr>
<td>Acid treated coke</td>
<td>8.0091</td>
<td>5.6016</td>
<td>4.72</td>
<td>87.78</td>
</tr>
<tr>
<td>Coke ash</td>
<td>2.0722</td>
<td>4.9354</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 6.2 shows the properties of coke, acid treated coke and coke ash made from the parent coke calcination. It was recognized from the table that metal oxides (minerals) contribute on lead and chromium adsorption. However, the acidic functional groups obtained through the modification of coke with acid and hydrogen peroxide prove to be more effective on Pb(II) removal at a chosen concentration compared to the rest shown in Table 6.2. The binding force of ash towards Pb(II) and Cr(III) shows that coke ash is more effective on Cr(III) than Pb(II). Elimination of minerals from coke proved to have enhanced adsorption strength when compared to coke ash which also played a role in the adsorption medium.
6.4 Conclusion

The adsorption characteristics have been examined at a constant parameters such as pH, initial concentration and time for the parent coke, functionalized coke and coke ash. Obtained results showed that each of the adsorbents showed some adsorption strength however the ash material had a minimal affinity towards the targeted heavy metals while the functionalized coke was more effective.
6.5 References


CHAPTER 7
GENERAL CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The purpose of this research was to prepare and characterize coke and coke-based composites for the removal of heavy metals in aqueous solution. The coke particles were separately modified through polymer coating with polymers such as polyvinyl alcohol, polyethylene glycol and polyvinyl pyrrolidone. Prior to polymer coating, coke was first subjected to hydrochloric acid for demineralization and also modified with hydrogen peroxide as an oxidizing agent. The prepared materials were then evaluated for their adsorption properties using Pb\(^{2+}\) and Cr\(^{3+}\) as ideal pollutants in aqueous solution. Throughout this report several outcomes were drawn which are summarized below:

- During the modification of coke powder with hydrochloric acid and hydrogen peroxide, the resulting ash content decreased from 15.04 to 4.72. On the other hand, the surface area increased by 8% upon modification. Newly formed active functional groups were seen on the FT-IR spectra and lastly the thermal stability was improved. Elemental analysis of the parent coke revealed high proportion of inorganic contents as compared to the modified coke where the carbon concentration was enhanced.

- Fusing coke and modified coke particles with hydrophilic polymers altered the surface properties of coke. Polymer films significantly blocked the pores that were present on coke especially on the parent coke where the minerals were also there and hindering the pores. SEM images also accord the coating of coke particles with polymers where it shows that parent coke roughness went smooth and homogenous after including polymers. The improved thermal stability obtained on acid treatment was maintained in this
step. Atomic ordering remained the same upon modification and through polymer coating.

- Adsorption studies revealed a marked adsorption capacity improvement on the coke hydrophilic polymer composites as compared to the parent coke and functionalized coke for the targeted metals. Cr$^{3+}$ was observed to have higher affinity than Pb$^{2+}$ for most adsorbent evaluated in this work.

- The Langmuir adsorption isotherm model showed higher correlation efficient values for most evaluated adsorbents as compared to the Freundlich isotherm model regardless of the measured heavy metal. Therefore the adsorption process of Pb$^{2+}$ and Cr$^{3+}$ could be best described by the Langmuir model in this study. As for the kinetic studies concern, pseudo second order was obeyed and could therefore be used to compute adsorption capacities for all the studied adsorbents.

7.2 Recommendations

The following recommendations are suggested for future investigations:

- The validation of the method used for preparation of the coke polymer composite, by varying the oxidizing agent concentration to get optimum active sites on coke. Even with changing the concentration values of the polymers to determine the optimal concentration.

- Application of the same adsorbents to real wastewater samples to observe the competing sites of the targeted metals with other metals that could be present in water.

- Desorption studies also need to be assessed to evaluate if the prepared composites could be regenerated for continuous use. This will be a confirmation that some active sites were not lost during the desorption process.