

SPENT FLUID CRACKING CATALYST (FCC) - A
POTENTIAL ADSORBENT FOR ORGANICS IN
HYDRAULIC FRACTURING FLOWBACK

By

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Abstract: Steady increase in the natural gas production in U.S.A. is mainly due to horizontal drilling and hydraulic fracturing (fracking) technologies. Three to five million gallons of water are used for fracking a well. Approximately, 30% of the water flows back to the surface after fracking a well, forming a huge waste stream. Also, disposal of flowback is a major barrier to the development of new shale gas plays. Spent fluid cracking catalyst (FCC), a refinery waste is proposed as an agent for treatment of flowback, another waste stream. Characteristics of fresh FCC, deactivation in FCC, properties of spent FCC are studied to enhance the understanding of the adsorption potential of spent FCC. Batch adsorption study is conducted to examine the adsorption of acetic acid, a very common organic in flowback, from aqueous solution with change in initial concentration and pH. Equilibrium adsorption data fit the Freundlich isotherm. Initial concentrations of acetic acid were selected from the typical concentration range in flowback, for the adsorption experiment. Adsorption capacity was observed to increase with increase in the initial concentration of acetic acid. Adsorption capacity decreased with increase in pH at 25 mg/L and 40 mg/L initial concentrations. The adsorption capacity change with pH is not monotonic at 10 mg/L and 55 mg/L concentrations. The primary adsorption mechanism is supposed to be through adsorption of undissociated acetic acid molecules on coke, matrix, and the Si=O=Si sites in the zeolite in spent FCC.

TABLE OF CONTENTS

Chapter	Page
I. INTRODUCTION	1
Hydraulic Fracturing and Flowback Water Treatment	1
Details about Water Usage in Fracturing.....	2
Other factors for flowback management.....	4
II. FLUID CRACKING CATALYST (FCC)	7
FCC Characteristics	7
Deactivation in FCC	10
Deactivation by coke.....	12
Types of coke	13
Coke Formation and Composition	16
Hydrothermal Dealumination	18
III. SPENT FCC	20
Properties of Spent FCC	21
Handling and disposal	23
Availability	24
Adsorption potential.....	25
IV. METHODOLOGY	28
Materials and Apparatus	28
Batch Adsorption Study.....	29
Concentration Analysis	32
Spectrophotometric method.....	33

Chapter	Page
V. RESULTS AND DISCUSSIONS	35
Adsorption with Change in Initial Concentration	35
Percentage Adsorption	41
Adsorption with Change in pH	45
VI. CONCLUSIONS AND FUTURE STUDY	51
REFERENCES	54
APPENDICES	62

LIST OF TABLES

Table	Page
3.1 Comparison of the properties of fresh and equilibrium FCCs	21

LIST OF FIGURES

Figure	Page
1.1 Typical water lifecycle at a frack job.....	3
5.1 Effect of acetic acid initial concentration on spent FCC adsorption capacity	35
5.2 Comparison of adsorption capacity with concentration for banana peels and spent FCC	37
5.3 Langmuir isotherm for the adsorption of acetic acid by spent FCC	38
5.4 Freundlich isotherm for adsorption of acetic acid by spent FCC	40
5.5 Change in percentage adsorption of acetic acid with initial concentration	41
5.6 Comparison of percentage adsorption change with initial concentration of acetic acid for spent FCC and silica gel	42
5.7 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 15 mg/L.....	47
5.8 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 25 mg/L.....	48
5.9 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 40 mg/L.....	48
5.10 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 55 mg/L.....	49

CHAPTER I

INTRODUCTION

Hydraulic Fracturing and Flowback Water Treatment

Since 2005, natural gas production in the United States (U.S.) has increased significantly (Accenture 2012). Since 2010, the U.S. is largest producer of the natural gas in the world (Bloomberg 2014). The increase in natural gas production is attributed to improvements in horizontal drilling and hydraulic fracturing (fracking) technologies to recover gas trapped in tight formations, such as shale. The “fracking” process requires significant quantities of water, which are injected into wells along with sand and specialized chemicals under pressure. Estimates put water usage between 3 and 5 million gallons for fracking a single well (Accenture 2012). Approximately, 140 billion gallons of water are used to fracture 35,000 wells in the United States each year (United States Environmental Protection Agency (US EPA) 2011). Though up to 30% of the used water can return to the surface during the fracking process within the first 10 days, this flowback water cannot be readily used due to contaminants such as formulation ingredients, organics, oil,

gas, salt and heavy metals (Wolford 2011). This contaminated water is typically disposed underground in EPA Class II salt-water injection wells.

Exploration and production companies are looking for ways to reduce the amount of fresh water used and to cut the high costs of hauling millions of barrels of water to oil and gas wells, and subsequently to underground disposal wells. Water management is one of the most challenging social issues facing current and future shale gas production (Schultz 2012). Two barriers to the development of new shale gas plays, related to the water handling and usage are:

1. Fresh water availability
2. Disposal options for the fracking flowback water

Details about Water Usage in Fracturing

In Texas, 26.6 billion gallons of water were used for fracking in 2011, and in one district in West Texas, the share of water resources used by fracking well sites jumped from 25% in 2010 to 40% in the first half of 2011 (Harkinson 2011). In Michigan, regulators granted a permit for a drilling company, Encana Oil and Gas, to use more than 21 million gallons of water at a single well in 2012 (Eco Watch 2014). Repeatedly siphoning off these large quantities of water for fracking can cause problems for local authorities to supply water for drinking and irrigation. The typical water lifecycle at a frack job is depicted in Figure 1.1.

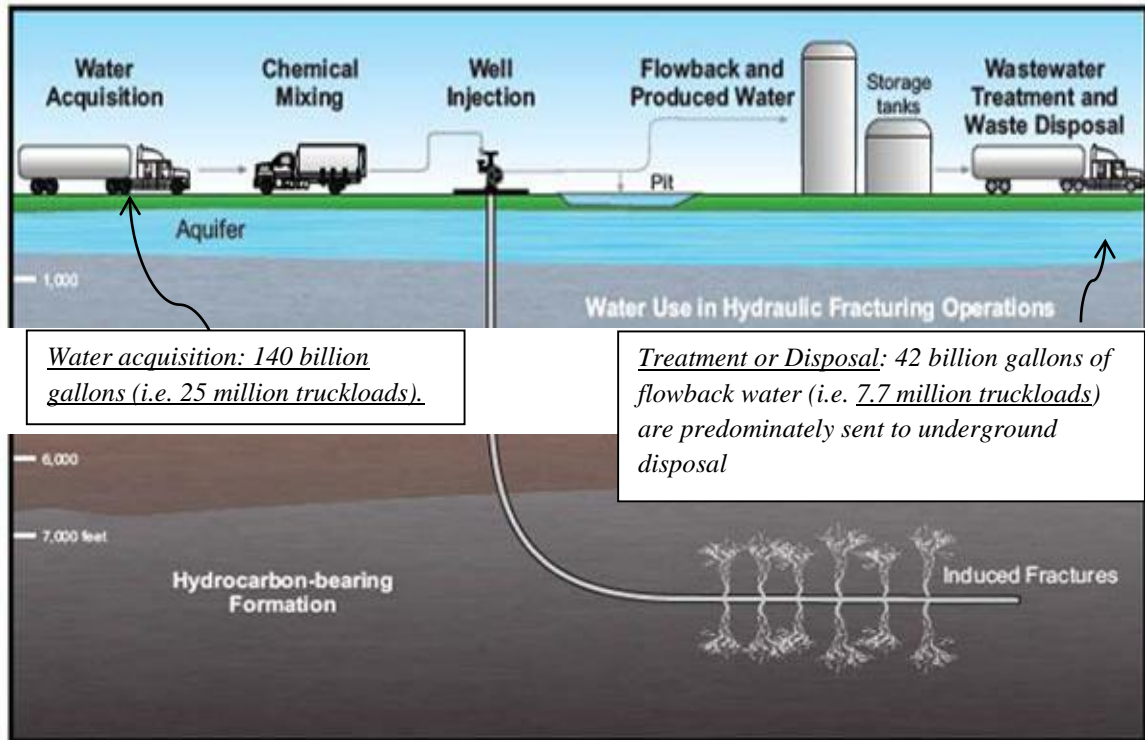


Figure 1.1 Typical water lifecycle at a frack job (United States. EPA, 2012, Public Domain image)

The overall amount of water used for fracking, even in drought-prone states like Colorado and Texas, is one percent, far less than agricultural or municipal uses (Galbraith 2013). Therefore, some studies concluded that the water usage does not affect the local water supplies (Freyman 2014). However, the data on overall water usage for fracking masks the significant effects on local water supplies. Some of the most oil-rich parts of Texas, including the Eagle Ford Shale and the Permian Basin, are also some of the state's driest areas. According to Freyman (2014), a county-by-county scale to capture the intense and short-term impact on water supplies helps in understanding the local effects. For example, in the Eagle Ford shale formation in South Texas, particularly in Webb County, one-third of the area's annual groundwater recharge is estimated water usage for fracking (Barringer 2013). In some oil-rich areas, like Dimmit County, the percentage of

water used for fracking has reached double digits and is growing along with the oil boom. The local effects in Texas have motivated the Railroad Commission, which regulates the oil and gas industry in the state, to encourage recycling by loosening rules governing that process (Galbraith 2013).

According to Freyman (2014), Colorado faces the most widespread potential conflicts between fracking and other water uses. Right now, oil and gas companies in Colorado pay more than 60 times the price paid by farmers for an equal amount of water (Healy 2013). Recently, Aurora, a suburb of Denver, approved a \$9.5 million deal to lease 2.4 billion gallons of effluent water to the Anadarko Petroleum Corporation (Healy 2013). This dynamic might be attractive to municipalities to strengthen their budgets by delivering water to industry at high prices. On the other side, local community might be worried that water resources will be exhausted or water will be unaffordable for the farmers.

Other factors for flowback management

Saving fresh water is considered the only objective for treating flowback by many studies (Acharya 2011). However, there are some other factors driving the necessity for treating the flowback including:

1. Prevention of Earthquakes.

Usage of disposal wells is very high in shale energy industry when compared to other industries that used disposal wells in the past (Freyman 2014). Research studies in Colorado, Arkansas, Ohio, Oklahoma and Texas suggested that the earthquakes occur due to frequent injection of frack flowback water in disposal wells (USGS (United States

Geological Survey) and Oklahoma Geological Survey 2013; National Research Council, 2012). According to USGS and Oklahoma Geological Survey 2013, Oklahoma used to experience one to three earthquakes a year, between 1978 and 2008. Since 2009, Oklahoma has experienced about 40 earthquakes a year. The drastic increase in seismic activity is closely related to the deep well injection of water from over 4,500 hydraulic fracturing wells across the state (USGS and Oklahoma Geological Survey 2013). According to a study by University of Oklahoma, Columbia University, and USGS scientists, the largest earthquake in Oklahoma history of a magnitude of 5.7 was likely caused by flowback injection into disposal wells (Leber 2012). In the statement issued by Emergency Operations Center, Stillwater, deep well injection is mentioned as one of the top reasons for the recent seismic activity in and around Stillwater (Hill 2014). If the flowback is treated instead of injection into disposal wells, seismic activity might be reduced (Leber 2012).

2. Disposal & transportation costs

Costs associated with injection-well disposal have increased steadily. Pennsylvania's Marcellus shale and the dry plains of western Texas are some of those areas where water and disposal costs can exceed \$1 million per well (Fuquay 2013).

Many times, the injection wells are located at least 25 miles away from the frack sites (Seth et al. 2013). This involves additional cost for water transportation from the frack site to the injection well. Presently, the transportation and disposal costs are up to 18 \$/barrel in some places (Seth et al. 2013). There are many sites in Ohio and Pennsylvania, which fall into this category (Freyman 2014). In those places, flow back treatment is more economical than underground injection.

Along with the cost of transport, there are concerns about safety during the transport of flowback water. The flowback contains hazardous and volatile chemicals (Wolford 2011), like acetic acid, benzene, toluene, ethyl benzene, and xylenes (BTEX). Any truck accident or leakage can cause adverse effects to environment like toxicity, and formation of photochemical smog (US EPA 2006).

CHAPTER II

FLUID CRACKING CATALYST (FCC)

FCC CHARACTERISTICS

Spent FCC is evaluated as an adsorbent to remove organics from hydraulic fracturing flowback in the present work. To understand how spent FCC has adsorption potential, the physical and chemical characteristics should be considered. FCC catalysts are fine particles with an average size of 60 to 100 μm . However, the particle size distribution is wide, ranging from 10 to 150 μm . They have a bulk density of 0.80 to 0.96 g/cm^3 . (Yang 2003)

According to Yang (2003), there are certain properties that are desired for FCC catalyst to ensure efficient operation of FCC unit: stability to high temperature and steam, high activity, large pore sizes, and good resistance to attrition.

The zeolites applied typically as FCC catalysts are Type X, Type Y and ZSM-5 (Venuto and Habib 1979). Types X and Y possess similar crystal structures but the X

zeolite has a lower silica-alumina ratio, which makes it less stable. ZSM-5 is a versatile zeolite that helps in increasing the yield of olefins from FCC. The NaY zeolites are often ion-exchanged with rare earth elements like lanthanum or cerium that form bridges with two or three acid sites in the zeolite framework. This protects the acid sites and also makes the zeolites hydrothermally stable. As the demand for gasoline with higher octane rating increases, ultra-stable Y or USY zeolites are being used to enhance olefinicity; and hence, the octane number of gasoline. These catalysts have higher silica to alumina ratios than conventional Y zeolites. There are four components in an FCC catalyst, viz., zeolite, matrix, binder, and filler.

Zeolite: Zeolite is the most important component in the catalyst; providing the majority of surface area for reaction and constitutes about 15 to 50 weight percent (Sadeghbeigi 2000). Zeolites are composed of silica and alumina tetrahedra with each tetrahedron having either aluminium or a silicon atom at the center and four oxygen atoms at the corners (Kulprathipanja 2010). Zeolite structure allows only a certain size range of hydrocarbon molecules to enter the lattice. Generally, molecules larger than 8 to 10 nm are unable to enter the zeolite lattice (Kogel et al. 2006).

The catalytic sites in the zeolite are acidic and contribute the majority of the catalytic activity. The acidic sites are provided by the alumina tetrahedra. The aluminium atom at the center of each alumina tetrahedra is at a +3 oxidation state. It is surrounded by four oxygen atoms of -2 oxidation state, at the corners of the tetrahedron. The oxygen atoms are shared by the neighbouring tetrahedra. Therefore, the net charge of the alumina tetrahedra is -1 which is typically balanced by a sodium ion during the production of the catalyst. The zeolite made by balancing of charges with sodium ions is not

hydrothermally stable. The ammonium ions are frequently used to replace the sodium ions. The drying of zeolite vaporizes ammonia and leaves behind H^+ ions. The H^+ ions provide the acid sites (both Brønsted acid and Lewis acid sites) necessary for cracking reactions (Venuto and Habib 1979).

The tetrahedral arrangement gives zeolites an open framework structure with a well-defined pore structure and high surface area. Rings of oxygen atoms determine the pore diameters in all zeolites. These pores cause diffusional limitations in zeolites. The sodalite units (or the truncated octahedral units) having the silica alumina tetrahedra are the secondary building blocks of the zeolites, used for catalytic cracking. Molecules pass through the twelve membered oxygen rings into these units.

Matrix: The matrix component of an FCC catalyst contains amorphous alumina and provides catalytic activity. The matrix helps in the cracking of larger molecules which cannot enter the pores of zeolite and also acts as a trap for metal contaminants present in the FCC feedstock that can affect the catalytic activity.

The surface area of the catalyst comes from the zeolite and the matrix. The combined area is around $800 \text{ m}^2/\text{gm}$ for conventional Y zeolites and around $600 \text{ m}^2/\text{gm}$ for USY zeolites (Sadeghbeigi 2000). The reduction in surface area is due to the hydrothermal treatment given to the zeolites to enhance their stability which affects their crystallinity and brings about changes in their pore structure.

Binder and Filler: The binder and filler components provide the physical strength and integrity of the catalyst. The binder is usually silica sol and is used to glue the zeolite, matrix and filler together. The filler is usually clay (kaolin). The clay is primarily used

to increase density and catalyst strength. Increase in catalyst strength decreases attrition resistance of catalyst (Sadeghbeigi 2000).

The FCC feed stocks typically contain metal contaminants like nickel, vanadium iron, activity and performance by catalysing undesirable reactions like dehydrogenation and condensation (polymerization). Nickel and vanadium are particularly troublesome (Sadeghbeigi 2000). Nickel catalyzes dehydrogenation reaction, removing hydrogen from stable compounds to form unstable olefins. These olefins polymerize to higher hydrocarbons. Vanadium also catalyzes dehydrogenation, however less than nickel. Vanadium's contribution to dehydrogenation reaction is 20-50% of nickel's contribution. However, vanadium migrates to the zeolite part of catalyst, unlike nickel. Thus vanadium affects the zeolite structure, and thereby the catalyst surface area and activity.

All FCC units withdraw some of the circulating equilibrium catalyst as spent catalyst. The withdrawn catalyst is replaced with fresh catalyst in order to maintain the desired activity level. The withdrawn catalyst is used as the adsorbent in the present work --after preliminary treatment. Details about the pre-treatment of the spent catalyst are described in the methodology section.

Deactivation in FCC

Catalysts deactivate due to two types of phenomena: physical and chemical. Examples of physical phenomena are sintering, occlusion, loss of active surface, among others. However, zeolite-based catalysts are designed such that they are normally stable enough to avoid these processes in the operating conditions. Therefore, chemical causes are the

main problem for the FCC deactivation. Chemical phenomena of deactivation can be classified into three categories (Cerqueira et al. 2008):

1. Chemical degradation

Chemical degradation involves reaction of a compound with the catalytic phase, causing loss of reactivity. The main agents are

- a. Alkaline metals: They neutralize the acid sites on the zeolite part in FCC
- b. Steam: Steam causes de-alumination and decrease the number of acid sites
- c. Vanadium (V): V destroys the zeolite framework.

2. Poisoning

Poisoning is an irreversible phenomenon resulting in permanent loss of the activity of FCC. It represents the adsorption of impurities on the catalyst active sites. Basic nitrogen compounds and coke are the major poisons in the FCC process. Coke on the spent FCC might be beneficial for adsorption of organics. Therefore, different types of coke are discussed in detail, later in this section.

3. Fouling

Fouling involves blocking the porous structure and access to active FCC sites. Deposition of coke and metals fall into this category (Froment 1980).

There is a different type of classification based on whether the deactivation is reversible or irreversible. In fluid catalytic cracking processes, regeneration is accomplished by combustion with air. Therefore, all the FCC deactivation phenomena can be classified into two types.

Deactivation by coke

The FCC deactivation by coke is caused either by poisoning of acid sites or by pore blockage (Forzatti and Lietti 1999). In the poisoning phenomenon, one coke molecule blocks one acid site. Thus the poisoning affects the catalyst activity linearly. Poisoning may also affect the reaction selectivity (Froment 1980). In the case of pore blockage, one coke molecule blocks the access of reactants to, on average, more than one active site. Therefore the deactivation effect is more pronounced in case of pore blockage.

From the acidity–activity correlations, the Brønsted acid sites located in the supercages of the zeolite are the main active sites for the cracking reactions. During coke formation, the activity of the USY zeolite varied linearly with the amount of Brønsted acid sites accessible to pyridine in the supercages (Caeiro et al. 2007). Prior to the blockage of pores, coke molecules can be distributed over the zeolite crystallites in a heterogeneous manner. The coke can be more concentrated at the external surface (pore mouth), reducing the effective pore diameter. In that case, the diffusion resistance of reactants in the crystallites increases (Hopkins et al. 1996).

Accessibility of reactant molecules to the active sites located inside the FCC is a very important parameter in the mass transfer. Either selected model molecules and catalyst components or with real feedstock and commercial catalysts can be used to estimate the accessibility. Zeolite crystallite size affects the amount of coke needed to partially block the access to zeolite pores. The higher the zeolite crystallite size, the less amount of coke is needed to cause partial blockage of the access to zeolite pores; small crystallites possess a much higher external surface area, hence limiting the pore blockage.

Coke tends to adsorb onto the acid sites in the zeolite (Cerqueira et al. 2007). Thus, coke deposits can severely reduce the accessibility to the acid sites. Cerqueira et al. (2007) mentioned that decrease in pore volume can be as high as twice the volume of the coke deposited. The matrix can trap the large molecules containing heteroatoms and contaminant metals, thereby reducing the amount of coke formed (Venuto and Habib 1979).

The coke deposits are not uniformly distributed in the FCC (Forzatti and Lietti 1999). The coke concentration profiles were studied by controlled combustion, electron microscopy techniques. The non-uniform distribution is related to the intra-particulate diffusional limitations. (Forzatti and Lietti 1999)

Types of coke

Coke is a highly carbonaceous material, typically constituting of poly-aromatic compounds. Generally, coke comprises of compounds with hydrogen to carbon ratio (H/C ratio) from 0.3 to 1.0 (Venuto and Habib 1979). There are five main types of coke identified in catalytic cracking (Cerqueira et al. 2008).

1. Catalytic coke:

Catalytic coke is formed when hydrocarbon is cracked via acid catalysis. It is a by-product of some undesirable condensation and dehydrogenation reactions.

2. Catalyst-to-oil coke:

This coke refers to hydrocarbons entrained in the small pores and not removed by the stripper. It is not actually coke as the H/C ratio is more than one. In the present work,

pre-treatment of adsorbent involves conversion of catalyst-to-oil coke to normal coke by pyrolysis. This is done as fresh coke has some adsorption potential for hydrocarbons (Zubot et al. 2012). The pre-treatment is discussed elaborately in the methodology chapter.

3. Thermal coke:

Thermal coke is formed by a free radical mechanism. It is formed at high reaction temperatures, favorable for the formation of free radicals. Hydrogen is also formed along with thermal coke. In the typical conditions of fluid catalytic cracking, there is low extent of thermal cracking. Hence, thermal coke is formed in lesser quantity, when compared to catalytic coke.

4. Additive coke:

Additive coke is formed from heavy hydrocarbons present in the feed. The amount of additive coke formed is related to Conradson carbon residue, the residue remaining after the fuel has been pyrolyzed (Cerqueira et al. 2008). Therefore additive coke is also referred to as Conradson coke.

5. Contaminant coke:

Contaminant coke is formed as a by-product from dehydrogenation catalyzed by Cu, Ni, Fe and V. The effect of Ni and V on activity of catalyst has been discussed earlier in the FCC section.

The different types of coke may not have influence the cracking activity in the same manner. The time-scale in which the deposition of different types of coke over the catalyst determines whether the deactivation mode is active site deactivation or pore

blockage. Feed composition, catalyst composition and process operation are the most important variables that affect the catalyst deactivation

Hollander et al. (1999) noted that there is significant residual activity on the coked FCC catalysts. Residual activity implies that the coked FCC catalysts have significant adsorption potential, as adsorption is the primary step in catalysis. Lee et al. (2004) observed the adsorption of p-xylene on coked FCCs. Liles and Schwartz (1976), and Sanga and Nishimura (1976) have reported usage of spent FCC as the adsorbent for water treatment. More discussion on the previous work on adsorption by spent FCC will be done in the “Spent FCC” and “discussion” sections.

Catalytic coke:

Formation of catalytic coke, the most important type of coke, depends upon four factors (Guisnet et al. 1997).

1. Feed properties:

The presence of alkenes and aromatics in the feed substantially increases the rate of coke formation (Cerqueira et al. 2008). Alkenes and aromatics have some degree of unsaturation due to the double bonds and rings. They have H/C ratio closer to that of coke. Reactions for formation of coke from aromatics and alkenes require fewer steps than formation from alkanes, due to the structural similarities. Therefore, the rate of coke formation is high in the case of feed with alkenes and aromatics. Coke formation mechanism is described later in this section.

2. Operating conditions:

High temperatures favour formation rate as activation energy is high for coking reactions (Froment 1980). The coke composition is similar to that of the reactants at low

temperatures. At high temperatures, coke composition does not depend up on the nature of the reactants. The coke is highly poly-aromatic at these conditions (Cerqueira et al. 2008).

3. Zeolite acidity:

As the acid site density increases, proximity of the acid sites increases and, hence, the coke formation rate increases.

4. Zeolite porous structure.

At high temperatures, pore structure has the greatest effect on the composition of coke. Reactants have little effect. If zeolite has small cages, smaller molecules like anthracenes or pyrenes are formed. Bulkier compounds are produced in the zeolites with large cages.

Coke Formation and Composition

Research has been going on in the last few decades to enhance the understanding of catalyst deactivation by coke (Froment 1980, Guisnet et al. 1997, Cerqueira et al. 2008). Chemical composition of coke is studied by means of spectroscopic techniques such as electron paramagnetic resonance (EPR), magic angle spinning ^{13}C nuclear magnetic resonance, ultraviolet (UV) and infrared (IR) spectroscopy, X-ray diffraction (XRD) and Raman spectroscopy (Li and Stair 1997). These methods typically require the complete removal of coke from catalyst.

A detailed characterization study of commercial spent FCC catalyst has shown that coke was mainly constituted of heavy condensed aromatic compounds. Typically, the carbon content in the spent FCC is in the range of 0.7-1.5 weight percent (Cerqueira

et al. 2008). Despite the high carbon content, commercial spent FCC catalysts have some residual catalytic activity.

Coke formation:

The mechanism of the coke formation consists of several consecutive reactions. The number of reactions depends up on the reactant molecule. The overview of the mechanism is presented here. Alkanes need to be cracked to produce olefins. They must be oligomerized to produce C₆ + alkenes. The C₆+ alkenes need to undergo hydrogen transfer reactions, forming dienes. These latter are to be converted into naphthenes, that must proceed via three more hydrogen transfer reactions forming aromatics, which are then converted into soluble coke. (Guisnet 1997).

For naphthenes the mechanism only involves the last two reactions. For aromatics, the mechanism consists only of the final step. This is the reason why aromatic content in the feed normally yields larger amounts of coke (Guisnet 1997).

There is good amount of literature (Guisnet 1997, Cerqueira et al. 2000, Cerqueira et al. 2008) on the supposed mechanism of hydrogen transfer in catalytic cracking that suggest that both the intra and intermolecular hydrogen transfers are possible. In fluid catalytic cracking, the focus has been on intermolecular processes. Any two organic compounds can undergo hydrogen transfer reactions if at least one of them is unsaturated. The mechanism of hydrogen transfer is complex (Cerqueira et al. 2008) and not relevant to the present study. Therefore, the mechanisms are not discussed.

The coke formation reactions are not complex after the production of unsaturated molecules like aromatics and olefins. Catalytic coke formed is typically poly-aromatic in

nature, implying that the first aromatic formation is important in coke formation reactions.

Hydrothermal Dealumination

FCCs are subjected to very high temperatures in the presence of steam during the reaction and regeneration steps in the fluid catalytic cracking. Therefore, the hydrothermal stability of zeolites, resistance to the combined effect of steam and temperature, is of paramount importance for catalyst manufacturers.

The standard USY zeolite, which is the main component of the FCC catalyst, possesses a framework with Si/Al ratio of approximately 5 (Cerqueira et al. 2008). During the regeneration, the zeolite rapidly undergoes dealumination. In fact, the zeolite in the FCC equilibrium catalyst possesses a framework with Si/Al ratio of approximately 20 (Cerqueira et al. 2008). The increase in Si/Al ratio from 5 to 20 makes the spent FCC more hydrophobic. When spent FCC is used as the adsorbent, the competition from water as an adsorbate with acetic acid in the acetic acid-water solution reduces due to the induced hydrophobicity.

As referred earlier, the reaction between the hydroxyl groups in the zeolite of FCC and steam causes dealumination and loss of acid sites at high temperatures. After dealumination, the zeolite becomes less acidic. However, the zeolite becomes more thermally and hydrothermally stable than the zeolite in the original catalyst. That is why, Y zeolites are usually steamed in optimized conditions before use in the FCC process

(Venuto and Habib 1979); the produced zeolite is generally denominated as USY (Ultra Stable Y). The Ultra Stable Y zeolite is the most stable version of Y zeolite.

CHAPTER III

SPENT FCC

In the previous chapter, the deactivation of FCCs was discussed; specifically how the activity of FCCs decreases. When the catalyst activity declines below an acceptable level, regeneration is required before reuse; however, regeneration is not always possible (Trimm 2001). After a few cycles of regeneration and reuse, the catalyst activity may decrease to very low levels and further regeneration may not be economically feasible.

In the present work, spent FCC was received from the Philips 66 refinery, Ponca City. The information on E-cat (Equilibrium catalyst) composition was not disclosed due to proprietary reasons. Therefore, typical properties of equilibrium FCCs are discussed in this chapter initially. Some of the properties contributing to adsorption potential of spent FCCs will be explained.

Properties of Spent FCC

Table 3.1 compares some of the properties of fresh, equilibrium catalysts with faujasite

type of zeolite (Venuto and Habib 1979). The chemical composition in the table is expressed in weight percentage (wt. %).

Properties	Zeolite		Amorphous Components	
	Fresh FCC	Equilibrium FCC	Fresh FCC	Equilibrium FCC
Alumina (wt %)	31	25.4	28	21.5
Carbon (wt %)	0	0.25	0	0.2
Sodium	0.04	0.04	0.03	0.02
Surface Area (m ² /g)	335	97	415	140
Pore Volume (cm ³ /g)	0.6	0.45	0.88	0.43
Particle Size of 0-20 µm (wt %)	2	0	2	0
Particle Size of 0-40 µm (wt %)	19	6	17	8

Table 3.1 Comparison of the properties of fresh and equilibrium FCCs; Source: Venuto and Habib 1979

Silicon to Aluminum (Si/Al) ratio:

Alumina is present in lesser quantities in equilibrium FCC than fresh FCC. Therefore, the Si/Al ratio is greater and hence, there would be more hydrophobicity. In the representation, the zeolite in the FCC has very low Si/Al ratio (~ 2.3) when compared to zeolites used in catalytic cracking like ZSM-5 (Si/Al ratio ~ 30-200) and USY zeolite (Si/Al ratio ~ 5) (Sadeghbeigi 2000). The zeolite present in equilibrium FCC with USY zeolite is close to 20 (Sadeghbeigi 2000). Therefore, the spent FCC in the table 3.1 is expected to adsorb organics to a lesser extent than that of spent FCC with ZSM-5 and USY zeolites. However, the low Si/Al ratio favors adsorption of metals (Álvarez-Ayuso

et al. 2003). The importance of Si/Al ratio in zeolites for organic removal from water was emphasised by de Ridder et al. (2012) in their work on removal of nitrosamines and pharmaceuticals from water. The relatively hydrophilic zeolites DAY and Mordenite 30 (Si/Al ratio- 30) were found ineffective for water treatment. The more hydrophobic zeolites ZSM-5 (Si/Al ratio- 80) and Mordenite 200 (Si/Al ratio- 200) were very effective as there was no competition from water to nitrosamines and pharmaceuticals for adsorption by the zeolites.

Carbon content:

There is some carbon (coke) on equilibrium FCC unlike fresh FCC. The coke introduces some hydrophobicity to the spent FCC. The hydrophobicity in spent FCC contributes to the favouring of adsorption of organic molecules (typically with lower polarity than polarity of water), over adsorption of water molecules (de Ridder et al. 2012).

Sodium content:

The sodium is present in low levels on equilibrium catalysts when compared to fresh catalysts. The presence of sodium in zeolite increases hydrophilic nature (Akbar et al. 2012). Effect on adsorption due to the presence of Na in zeolite is discussed in the “Results and discussions” chapter.

Surface area:

Surface area of equilibrium fresh catalyst is around 1/3 that of fresh catalyst (Figure 3.1). Initial decrease in surface area is likely caused by the collapse of small matrix pores to become larger pores (Venuto and Habib 1979). The partial destruction of the zeolite cage structure due to the hydrothermal treatment is a major cause for the surface area reduction.

Pore volume:

There is reduction in pore volume. Due to the hydrothermal treatment, the zeolite structure is partially destroyed, and hence, the number of pores is reduced. Reduction in number of pores is one cause for reduction in the pore volume. Another cause is blocking of the pores by coke. Pore blockage by coke is discussed in the “Deactivation by coke” section in Chapter II.

Particle size distribution:

The finest particles of the catalyst used in the catalytic cracking unit are lost on the initial cycles of operation as particulate emissions (Venuto and Habib 1979). In the table 3.1, particles of 0 to 20 μm are not present in the equilibrium FCC. Also, particles of 0 to 40 μm are lesser in quantity in equilibrium FCC, when compared to fresh FCC.

Handling and Disposal

Most of these spent catalysts have been disposed of as landfill in approved dump-sites. Recently, spent FCCs have been used for low end uses in cement production and ultimately disposed of. Due to presence of Co, Ni, V, and other metals in spent FCC, it is considered as hazardous waste. Therefore, Spent FCC disposal must accord with the environmental regulations.

The environmental regulations regarding spent catalyst disposals have been becoming more stringent, as indicated by listing of spent hydroprocessing catalysts as hazardous wastes in June, 2000 (Rapport 2000, US EPA 2003). Spent FCC disposal falls under the purview of the Environmental Protection Agency (EPA), Basel Convention and

Organization for Economic Co-operation and Development (OECD) regulations (USEPA 2003). Proper handling and disposal of FCCs is a problem of huge concern in the petroleum refining industry due to the large amount of FCC waste generated and landfilling costs of 200 \$/tonne (Marafi and Stanislaus 2008). The last option for spent FCCs is disposal in dump sites since there is a steady increase in costs associated with landfilling (Chang 1998).

Other uses of spent FCCs may be attractive options, considering environmental regulations and economic benefits. In the present study, spent FCC is proposed as an agent for treating flowback, owing to its availability and adsorption potential. The proposed method uses a waste (spent FCC) to treat another waste (flowback from hydraulic fracturing). This will help towards the reuse of flowback, saving huge amounts of water, and the extension of service life of spent FCC, simultaneously.

Availability

Due to the demand for high quality transportation fuels and changes in the feedstock, the demand and, therefore, supply of FCCs has increased significantly. The amount of spent FCC available is not readily known from the literature. However, it can be estimated using the data on fresh FCC produced.

The major FCC suppliers in the world are W.R. Grace, Albemarle and BASF. CCIC in Japan, China's Sinopec and Petrochina are major suppliers of catalysts in their regions. Global supply of FCC catalyst is estimated at about 2,300 metric tons per day \pm 15% (Letzsch 2010). Using these data, around 700,000 tons of FCC catalyst are produced

annually and supplied to catalytic cracking units. The amount of spent FCC discharged from different catalytic cracking units depends upon the fresh catalyst quantity used, the catalyst life and the amount of deposits formed on them. Approximately, 50%, 350,000 tons, of spent catalyst is available for disposal, every year. More than half of the spent catalyst is disposed in the U.S.A. (Letzsch 2010)

Adsorption potential

Every catalyst needs to have adsorption potential for good activity. This is because the primary step in a catalytic reaction is the adsorption of reactant molecules on to the catalyst. Therefore, FCCs possess adsorption potential for the reactants (hydrocarbons) in the fluid catalytic cracking unit. As discussed, the hydrophobicity of spent FCC is due to high Si/Al ratio and coke.

Metal adsorption:

Sanga and Nishimura (1976) patented a process for preparation of a waste water treatment agent from spent FCC to remove heavy metal and ammonium ions from sewer water. The spent FCC was treated with sodium hydroxide (NaOH) under controlled conditions. The sodium content in the spent FCC is low and; hence, so is the cation exchange capacity. The treatment with NaOH is done so as to impart cation exchange ability, so that Na can be exchanged with heavy metals. Harandi (1994) developed a process in which refinery sludge is de-metallized by using spent FCC. Hot E-Cat, which is removed from the regenerator, is used here.

Japtiwale (2013) reported adsorption of Cu on spent FCC. He observed the maximum adsorption capacity of 4.7 mg/g at pH near 6. Here, the spent FCC was used without any kind of chemical or thermal treatment. Shuqin et al. (2010) modified FCC, by washing with HCl solution (0.4-16 %) for 2.5 hours at 80⁰ C, and used it to adsorb Cu²⁺ from water. They observed maximum adsorption capacity of 26 mg/g near pH 5. The higher adsorption capacity might not be just due to the pretreatment. It could also be due to the difference in type of FCC used. With Ni²⁺ and Zn²⁺, they observed adsorption capacities of 24 and 17 mg/g. respectively.

Adsorption of organics:

In a patent by Liles and Schwartz (1976), spent cracking catalysts (zeolites) containing V, Fe, Ni, Cu and/or C were used for biological treatment of waste water from municipal and industrial sources. Here, the spent FCC was combined with activated sludge and the waste water was subjected to contact with the sludge at conditions of biological oxidation. The rationale was to increase the rate of biological oxidation by the introduction of inorganic oxides (from spent FCC) into the sludge. Liles and Schwartz observed an additional 8-18 mg/l removal of organics from different waste water samples.

Gong (2011) reported the removal of naphthenic acid from waste water using an agent comprising of zeolite and carbon in a U.S. patent. Approximately seven litres of the model waste water (essentially of 1000 ppm naphthenic acid in water) at 15-20 ml/min was subjected to contact with approximately 30 grams of agent (zeolite with 0.07 % carbon) in a column at 20° C. Around 15% of naphthenic acid was removed. The treatment agent was prepared by catalytically cracking fresh FCC with a hydrocarbon.

He mentioned that spent FCC has a composition similar to the treating agent and the treatment using spent FCC will be very cost-effective.

Blankson (2012) used modified spent FCC as a catalyst for the Catalytic Wet Air Oxidation (CWAO) process. They have concluded that the spent FCC is a good adsorbent of phenol after identifying the suitable conditions for the usage of spent FCC in the process.

CHAPTER IV

METHODOLOGY

Before discussing the methodology in detail, the main apparatus and reagents used are described.

Adsorbent: Spent Fluid Cracking Catalyst (FCC)

Spent FCC was received from the Philips 66 refinery in Ponca City, Oklahoma. Spent FCC was heated to 1000°C in a furnace (Thermolyne, Sybron Corporation, Iowa), before using as the adsorbent.

Adsorbate: Acetic acid (CH_3COOH)

Acetic acid was selected as the target adsorbate as it is the organic with highest concentration in Marcellus shale flowback (Wolford 2011). Acetic acid is used in the fracking fluid as pH adjusting agent, and sometimes as an iron control agent. Glacial acetic acid from Fisher Scientific, Fair Lawn, NJ was used for preparing acetic acid-water solutions of different concentrations.

Adsorption:

A magnetic stirrer (Thermolyne, Sybron Corporation, Iowa) was used to facilitate contact between adsorbent and acetic acid solution.

Concentration Analysis:

UV-V is spectrophotometer (Hach Company, Loveland, CO Model # DI/2010) was used to measure concentration of acetic acid.

Batch Adsorption Study**Pre-treatment of adsorbent:**

Spent FCC has some hydrocarbons, which are potentially strippable. These hydrocarbons are referred to as cat-to-oil coke although they are not actually coke. They can be converted to coke by heating and limiting the supply of air. Coked FCC is expected to adsorb organics better than the original spent FCC. This is because; the additional coke formed on the catalyst is a hydrophobic adsorbent and helps in favoring adsorption of organics over adsorption of water (Zubot et al. 2012). Coking of spent FCC is done before introducing the catalyst as an adsorbent by these steps.

1. Ten grams of spent FCC are placed in a Vitreosil crucible.
2. The crucible is placed in a furnace and heated to 1000°C for three minutes. The crucible is covered with a lid so as not to allow air. Partial combustion of the adsorbed organics on spent FCC results in additional coke deposits. Coke formation occurs around 1000°C (Bayratkar 2002).
3. The crucible is cooled to room temperature over two days.

4. The final weight of the crucible is recorded. No change in the weight confirms that no coke was burnt from the FCC, forming CO_2 or CO .

Adsorption experiment:

Acetic acid-water solutions are prepared with the following compositions: 15, 25, 40, and 55 mg/L. These concentrations are selected from the typical range of acetic acid in the flowback (Wolford et al. 2011). The concentrations were checked with spectrophotometer. The concentration measurement is described in detail in the next section.

1. One hundred milligrams (0.1 g) of spent FCC particles are placed into one hundred millilitres (0.1 L) of each solution. The mixture of FCC and acetic acid solution will be referred to as a “mixture” in this section. Each mixture is stirred on a magnetic stirrer to allow proper contact between adsorbent and the solution.
2. After 15 hours of stirring each mixture, the concentration of acetic acid is measured with a spectrophotometer every hour, until absorbance remains constant.
3. When the concentration of the acetic acid remains constant the mixture is removed from the magnetic stirrer. Also, there was no significant change in pH after adsorption. Measurements of pH are made with a benchtop pH meter (Oakton, Vernon Hills, IL, Model # PC 700).
4. The amount of adsorbed acetic acid from each mixture is calculated by multiplying the difference in concentration of acetic acid with the volume of the solution.

Adsorption capacity of spent FCC catalyst for each solution is obtained by dividing the amount of acetic acid adsorbed by the weight of spent catalyst. Steps 1-4 are

referred to as “adsorption experiment” in this chapter. Effect of initial concentration on adsorption was determined by the adsorption experiment here.

Adsorption with variation in pH

Acetic acid solutions of 15, 25, 40, and 55 mg/L are prepared. Variation of pH of each solution used HCl (0.001 and 0.002 M) and NaOH (0.001 and 0.002 M) standard solutions. Note that HCl and NaOH are key components of fracking fluid as well as flowback (Wolford, 2011). HCl is used in the fracking fluid to dissolve minerals and initiate cracks in the rock. NaOH is used to adjust pH in the fracking fluid so as to maintain the effectiveness of other components such as crosslinkers. Crosslinkers are used to maintain fluid viscosity as temperature increases. Viscosity of borate crosslinked fluids (crosslinkers) decreases as the pH decreases. NaOH increases the pH when the pH decreases. (Schultz 2011).

1. The pH values of 15, 25, 40, and 55 mg/L acetic acid-water solutions are measured with a pH meter (Oakton, Vernon Hills, IL, Model # PC 700). The pH values were observed as 4.2, 4.1, 4.0 and 3.9, respectively.

The aim of this experiment is to define adsorption while changing the pH at each of the four initial concentrations of acetic acid. Adsorption capacity is already calculated for each concentration at each initial pH. Therefore, adsorption capacity at the other three pH values are needed for each concentration.

2. Acetic acid solution (15 mg/L) is placed in a beaker with a magnetic stirrer. The initial pH of 15 mg/L acetic acid solution is 4.2. The pH is decreased to 4.1 by

- adding HCl, drop by drop, to the solution and monitoring the pH while stirring. The pH probe was kept in the solution with the help of a stand to easily monitor the pH. Changes in pH throughout this work are made in this manner, except that NaOH is used to increase the pH.
3. Adsorption experiments were performed with the 15 mg/L solution at pH of 4 and 3.9.
 4. Similarly, adsorption experiments used 25, 40 and 55 mg/L acetic acid at 4.2, 4.0 and 3.9 initial pH.

Concentration Analysis

A colorimetric method is used to measure the concentration of acetic acid in water. The method is an adaptation from the determination of organic acids in sewage liquid liquor, proposed by Montgomery et al. (1962). The method is based on the colorimetric ferric hydroxamate reaction for determining carboxylic esters. It is convenient and economical, when compared to distillation method of Frook and DiLallo and Albertson's titration method (Montgomery et al. 1962). Only, 0.5 mL of supernatant from the acetic acid-water-FCC mixture is needed for the concentration analysis. Also, the sample is undisturbed after analysis, unlike chromatography. Thirteen ppm acetic acid solution concentration is the detection limit for this method (Montgomery et al. 1962).

Sampling

When the adsorption equilibrium is reached, the mixture is kept undisturbed to allow the settling of FCC particles. Settling required 24 to 32 hours. Then, 10 ml of supernatant is

passed through laboratory filter paper (Whatman filter Paper Grade 1) to remove the adsorbent. The permeate is collected for concentration measurement.

Spectrophotometric Method

The concentration is determined, using an UV-Vis spectrophotometer at 495 nm wavelength (Montgomery et al., 1962). The sample, containing acetic acid, is heated with ethylene glycol and sulphuric acid to form esters viz., ethylene glycol mono-acetate and ethylene glycol di-acetate. Then, the mixture is reacted with hydroxylamine to form hydroxamic acids. Hydroxamic acids are converted to ferric complexes. The method is described in detail, here.

1. 0.5 mL of deionized water (DI water) is pipetted into a dry 25 mL sample cell with an adjustable volume pipetter (Fisher Scientific, Waltham, MA Model# Fisherbrand™ Finnpipette™ II).
2. 0.5 mL of filtrate is pipetted into another dry 25 mL sample cell.
3. 1.5 mL of ethylene glycol is pipetted into each cell.
4. 0.2 mL of 19.2 N sulfuric acid standard solution is pipetted into each cell. Sulfuric acid acts as a catalyst in esterification reactions.

Both the cells are swirled to allow mixing.

5. The samples in both cells are heated to 80°C in a 600 mL beaker on a hot plate.
6. After 3 minutes, both cells are cooled to room temperature by running under tap water.

Cells are swirled after performing each of the following steps:

7. 0.5 mL of hydroxylamine hydrochloride solution is pipetted into each cell.
8. 2 mL of 4.5 N sodium hydroxide standard solution is pipetted into each cell.
9. 10 mL of ferric chloride sulfuric acid solution is added to each cell. 10 mL of deionized water is added to each cell. Cells are swirled for three minutes. Ferric complexes are formed from hydroxamic acids. Few bubbles are also observed.
10. After 3 minutes of swirling the cells, the spectrophotometer is set to wavelength of 495 nm, and zeroed with blank in the calibrated program for acetic acid concentration measurement. The procedure for calibration of acetic acid concentration is explained in Appendix 1.
11. The sample is placed into the cell holder within the spectrophotometer. The final concentration of acetic acid is noted. The sample color was purple and stable for around 7-8 hours after the experiment. Then, the color of the sample started to reduce slowly.

CHAPTER V

RESULTS AND DISCUSSIONS

Adsorption with Change in Initial Concentration

The adsorption capacity data of spent FCC, with change in initial concentration of acetic acid in the solution is depicted in the Figure 5.1.

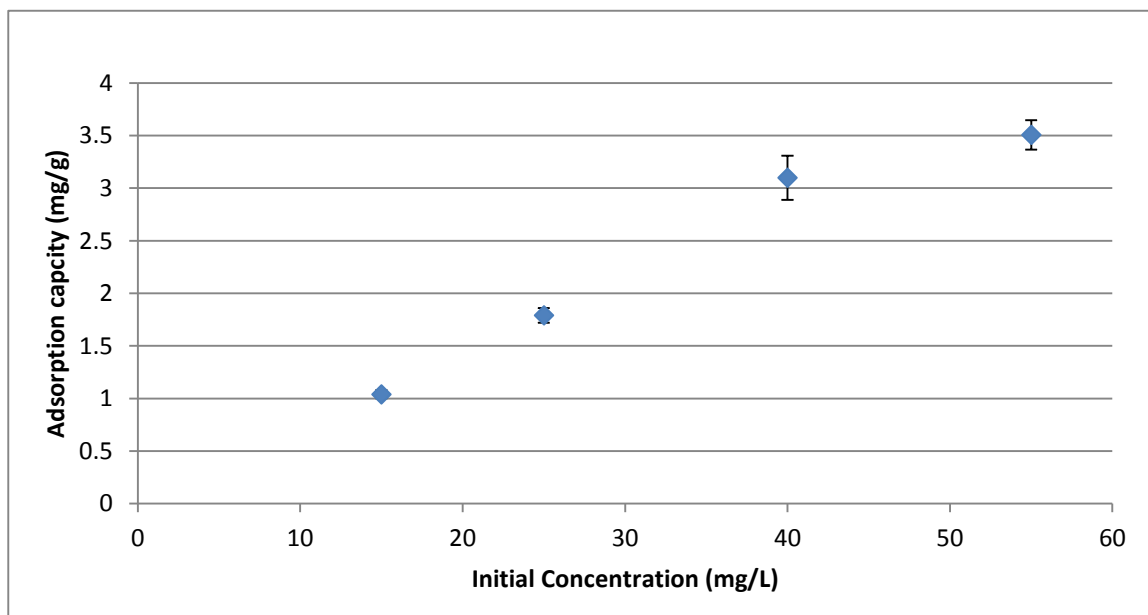


Figure 5.1 Effect of acetic acid initial concentration on adsorption capacity of spent FCC

From Figure 5.1, the adsorption capacity (Q_e) of spent FCC increases with the initial concentration of acetic acid (C_i). As the concentration of acetic acid is increased, the number of molecules of acetic acid per unit volume of solution is increased. In a solution with a higher concentration and same amount of adsorbent (spent FCC), there is more adsorbate (acetic acid) present in a unit volume of solution. There is more contact between adsorbent and adsorbate with an increase in concentration. Therefore, the adsorption capacity (adsorbate adsorbed/g of adsorbent) is increasing with concentration.

Abbasi and Alikarami (2012) observed the same trend in their work on adsorption of acetic acid by banana peels. However, the rate of increase of adsorption capacity with respect to initial concentration of acetic acid for banana peels is higher than the rate for spent FCC.

In the experiment by Abbasi and Alikarami (2012), banana peels were first separated gently from the fruit and washed thoroughly. Later, they were dried in sunlight for five days and in an oven at 70°C. The peels were chopped into small pieces and ground to 200-400 μm size before used for adsorption. Adsorption capacities of 1, 1.9, 3.5, 5.7 and 9.9 mg/g were observed with initial concentrations of 2, 4, 8, 15 and 30 mg/L. The maximum rate of change in adsorption capacity with concentration change was observed at initial concentration change from 2 to 4 mg/L. (Abbasi and Alikarami 2012)

The change in adsorption capacity with concentration for spent FCC and banana peels (Abbasi and Alikarami 2012) is compared in Figure 5.2. The adsorption capacity of banana peels is higher than that of spent FCC at the same initial concentration of acetic acid. At 15 mg/L acetic acid initial concentration, adsorption capacity is measured for

both the adsorbents. At that concentration, adsorption capacity of banana peels is approximately six times the adsorption capacity of spent FCC.

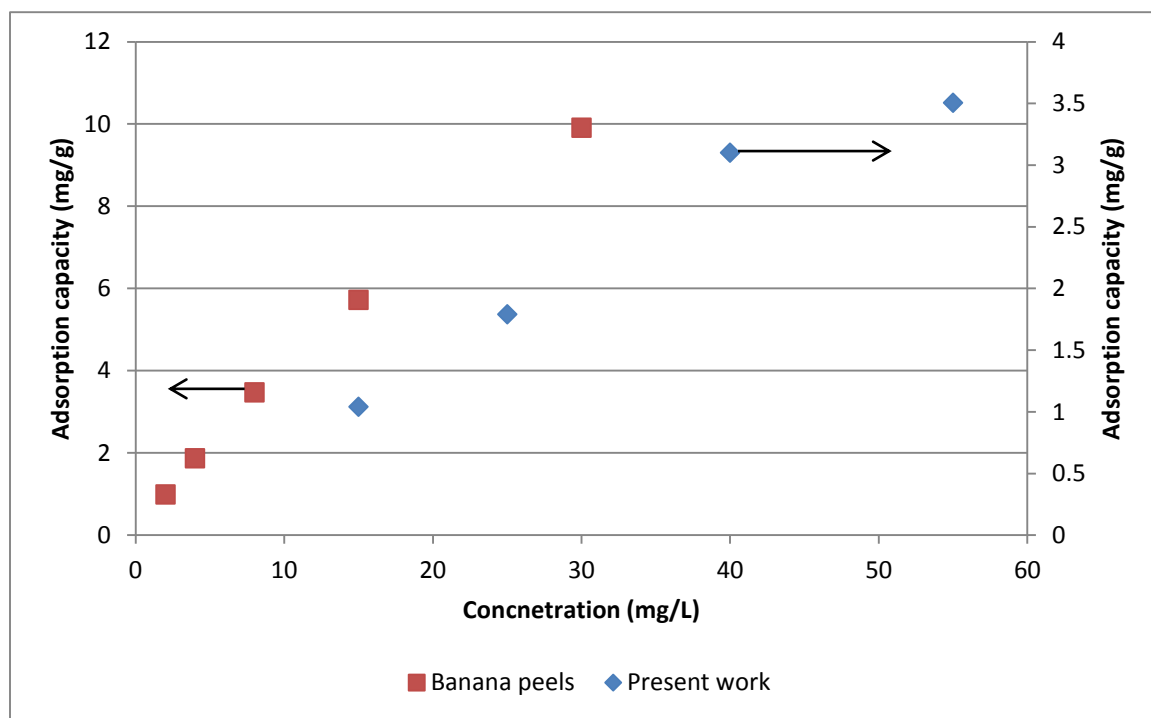


Figure 5.2 Comparison of adsorption capacity with concentration for banana peels and spent FCC. (Data obtained from Abbasi and Alikarami (2012); Adsorbent: Banana peels)

Dina et al. (2012) noted that the adsorption of acetic acid by activated carbon, made from maize cob derivatives, increased with initial concentration of acetic acid. Initial concentration was varied between 0.42 and 2.40 mg/L in this experiment. The experimental data fitted Langmuir and Freundlich isotherms.

Equilibrium adsorption experiments in the present work resulted in capacity data for spent FCC. However, the equilibrium relationship between spent FCC (adsorbent) and acetic acid (adsorbate) is best depicted by Langmuir and Freundlich isotherms which are commonly applied to the adsorption of organics. The adsorption data are analyzed with both the Langmuir and Freundlich equations.

Langmuir isotherm:

The Langmuir isotherm (B. Crittenden and W.J. Thomas 1998) is expressed as:

$$Q_e = Q_0 b C_e / (1 + b C_e) \quad (5.1)$$

Where

Q_e is the amount adsorbed at equilibrium (mg/g),

C_e is the equilibrium concentration (mg/L),

b is a constant representing the net enthalpy of adsorption (L/mg), and

Q_0 is the mass of adsorbed solute required to saturate a unit mass of adsorbent (mg/g).

Langmuir isotherm assumes that the adsorption occurs on localized sites with no interaction between adsorbate and maximum adsorption occurs when the surface is regular and covered by a monolayer of adsorbate.

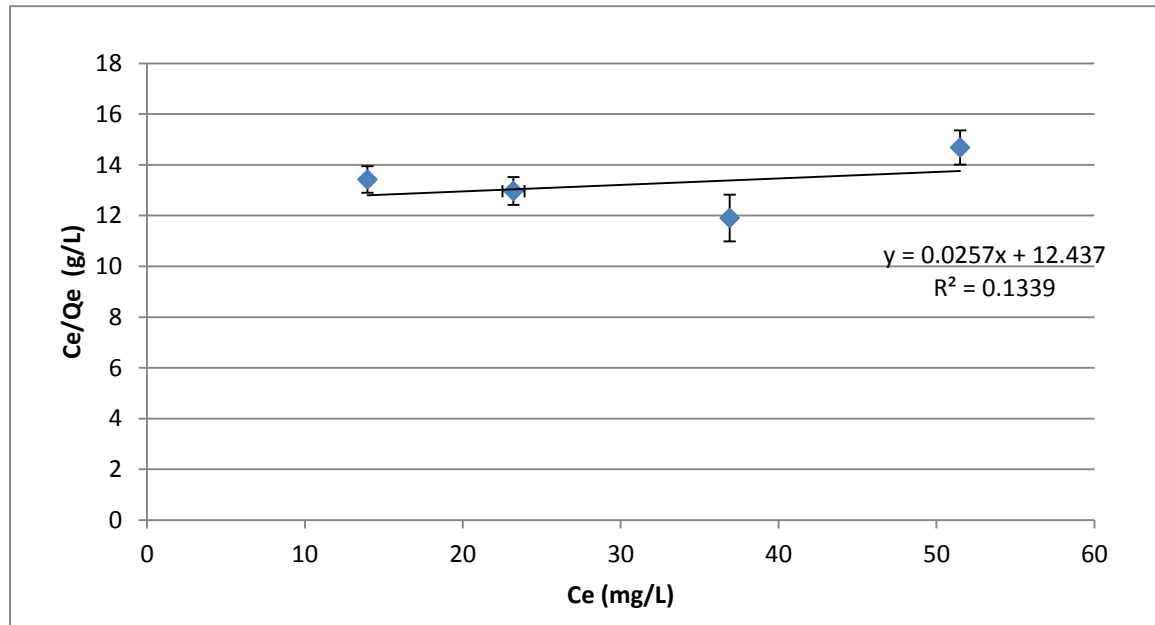


Figure 5.3 Langmuir isotherm for the adsorption of acetic acid by spent FCC

The Equation (5.1) is linearized and displayed below:

$$C_e/Q_e = (1/Q_0 b) + (C_e/Q_0) \quad (5.2)$$

C_e/Q_e is plotted against C_e , and linear regression is in Figure 5.3. The correlation factor (R^2) is 0.14, very much less than 1; implying not a good fit. Therefore, Langmuir isotherm does not describe the adsorption of acetic acid by spent FCC. Coke on the spent FCC, a major adsorption site, is not uniformly distributed and hence the adsorbent is not a regular surface. As one of the assumptions of the isotherm is not satisfied by the adsorbent, misfit of the adsorption capacity data to the isotherm is acceptable.

Freundlich isotherm:

The Freundlich isotherm model, which assumes that the adsorption occurs on heterogeneous surfaces, is often expressed as;

$$Q_e = K (C_e)^{1/n} \quad (5.3)$$

Where K is the Freundlich isotherm constant, and is the adsorption capacity at unit concentration; n is the Freundlich isotherm exponent, and represents the strength of adsorption. n should be greater than one for the equation to be valid (B. Crittenden and W.J. Thomas 1998). Due to the heterogeneous distribution of coke in spent FCC, spent FCC can be considered a heterogeneous surface. Adsorption data are expected to fit the isotherm.

Freundlich equation can be described by the linear form below:

$$\ln Q_e = \ln K + (1/n) \ln C_e \quad (5.4)$$

$\ln Q_e$ is plotted against $\ln C_e$, and the data is linearly regressed (Figure 5.4). A straight line fit into the data very well, as indicated by the correlation factor (R^2) close to one ($R^2 = 0.9766$). Therefore, Freundlich isotherm describes the adsorption of acetic acid by spent FCC, well.

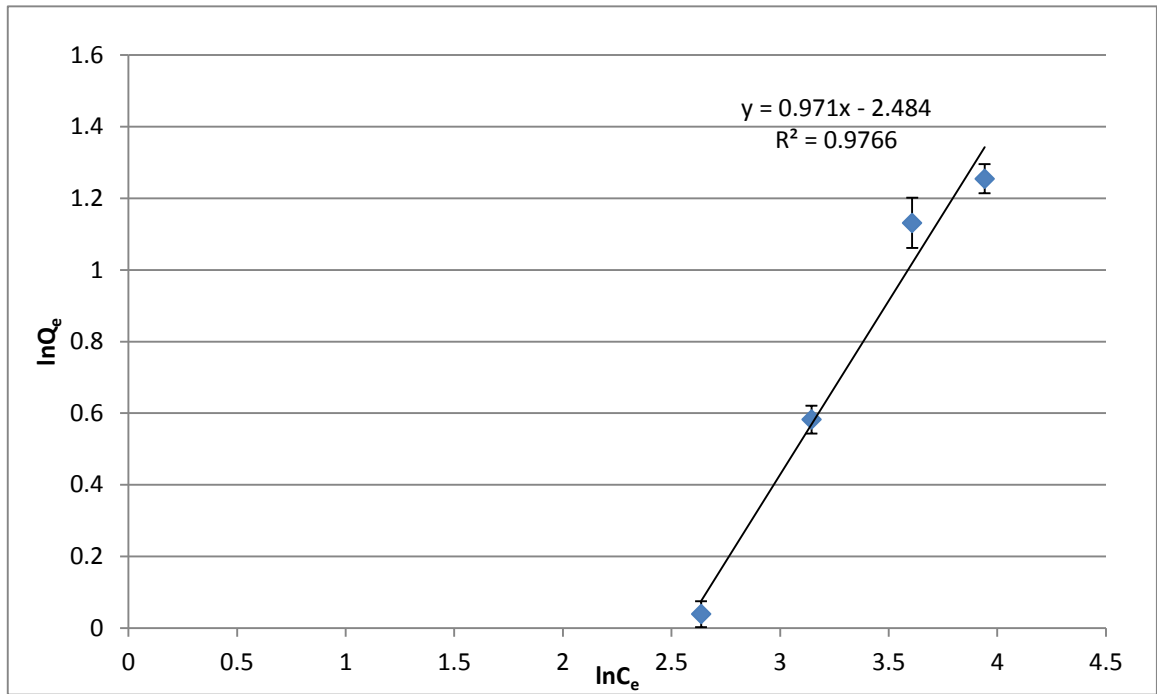


Figure 5.4 Freundlich isotherm for adsorption of acetic acid by spent FCC

The intercept and slope of plot of $\ln Q_e$ vs $\ln C_e$ is used to calculate the values of K and n .

Equation of the regression line is

$$y = 0.971x - 2.484 \quad (5.5)$$

Comparing the equations 5.4 and 5.5, we get

$$1/n = 0.971; \ln K = -2.484$$

From the calculations, the values of Freundlich equation constants are:

$$n = 1.030; K = 0.083 \text{ mg/g}$$

n value of greater than 1 indicates that the Freundlich isotherm is valid for the data.

Therefore the Freundlich equation for adsorption of acetic acid by spent FCC is

$$Q_e = 0.083 * C_e^{(0.971)} \quad (5.6)$$

Percentage Adsorption

Percentage of adsorbate adsorbed is considered as an important factor in evaluating the adsorption potential. The change in percentage adsorption of acetic acid with increase in concentration is in Figure 5.5. The percentage adsorption increases with concentration up to 40 mg/L and decreases with change in concentration from 40 mg/L to 55 mg/L. The initial amount of adsorbate affects the fraction adsorbed along with the amount of adsorbed species.

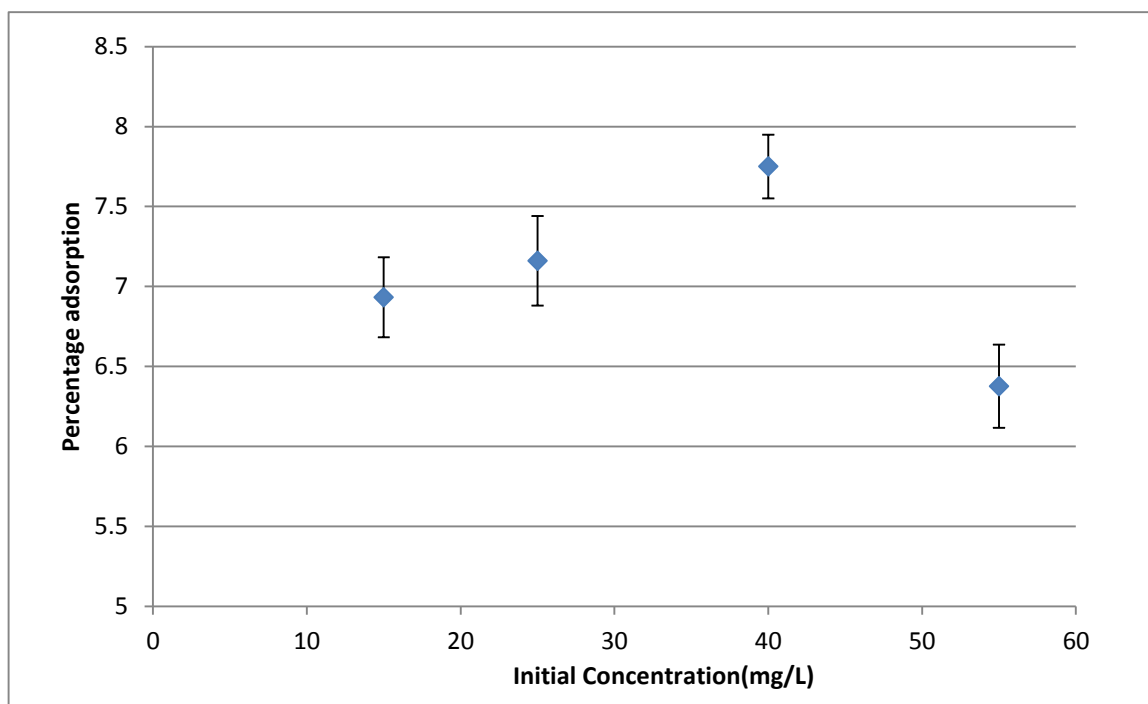


Figure 5.5 Change in percentage adsorption of acetic acid with initial concentration

As the concentration increases, there is increase in adsorbed species, as well as the increase in the initial amount of adsorbate. Thus, the change in percentage adsorption with increase in concentration is not monotonic, unlike the change in adsorption capacity with concentration.

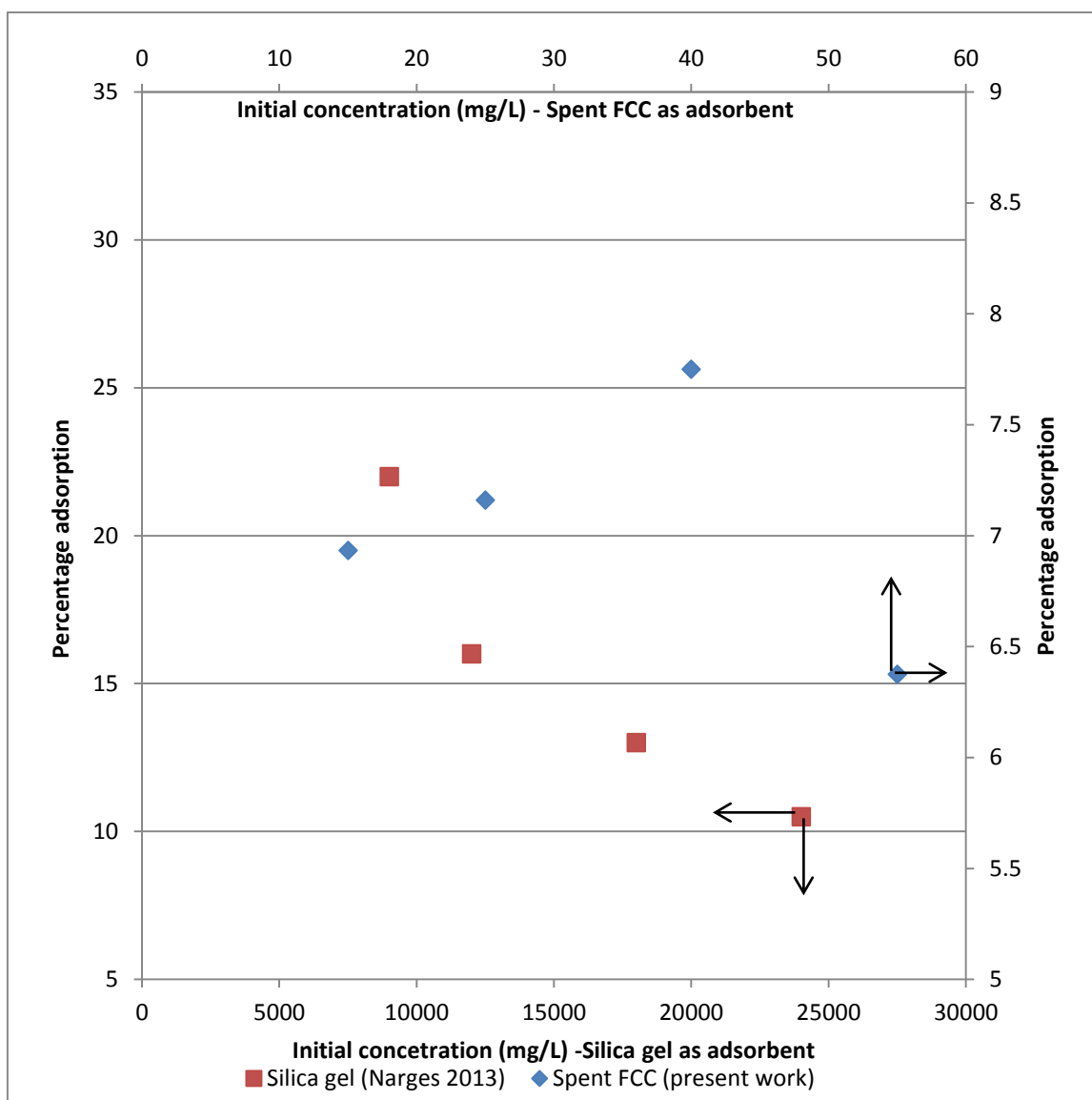


Figure 5.6 Comparison of percentage adsorption change with initial concentration of acetic acid for spent FCC and silica gel (Narges, 2013; Adsorbent: Silica gel

Narges (2013) observed a different trend in the change in percentage adsorption with initial concentration of acetic acid, while using silica gel as adsorbent. Change in percentage adsorption with increase in initial concentration of acetic acid is compared for spent FCC and silica gel as adsorbents in the Figure 5.6.

Percentage adsorption always decreased with increase in initial concentration for silica gel, unlike the case of spent FCC. Narges varied the initial concentration of acetic

acid between 9 and 24 g/L whereas the initial concentration range in the present work is 15-55 mg/L. Initial concentration ranges of Narges' work and present work do not coincide. The difference in trends in percentage adsorption might be due to the different initial concentration ranges used in the two works, large initial concentration range used by Narges (2013).

Adsorption mechanism:

Adsorption of acetic acid on any adsorbent can take place two ways (J.J. Kipling 1948).

They are

1. Adsorption of acetate ions
2. Adsorption of undissociated acetic acid molecules

The pKa value of acetic acid is 4.76 (Goldberg et al. 2002). Hence, the dissociation constant value is equal to $10^{-4.76}$, which is equal to 1.74×10^{-5} . From the dissociation constant value, only around 0.4% of acetic acid molecules dissociate in water, at room temperature. The fraction of dissociated acetic acid molecules and hence, the acetate ion concentration in the solution, is very less. Specifically, in 15 mg/L of 100 ml acetic acid solution, the quantity of dissociated acetic acid is around 0.006 mg. In this work the adsorbed quantity of acetic acid by spent FCC is to 0.104 mg for an initial concentration of 15 mg/L. The adsorbed quantity is about seventeen times the dissociated acid quantity. The ratio of adsorbed and dissociated acid is high for other concentrations as well, at which the adsorption experiment is conducted. Even if all the acetate ions get adsorbed by the spent FCC, the predominant adsorption route would be through undissociated molecules of acetic acid. Therefore, physical adsorption is the major type of

adsorption taking place in this case. There are three major sources of adsorption sites for organic molecules in the spent FCC. They are

1. Coke (Zubot et al. 2012)
2. Hydrophobic $\text{O}=\text{Si}=\text{O}$ sites of zeolite (Akbar et al. 2008)
3. Matrix (Venuto and Habib, 1979)

Coke is present on the matrix, and the zeolite pores of spent FCC. To get adsorbed on the coke inside the pores of zeolite and the hydrophobic sites of zeolite, acetic acid needs to enter the zeolite pores. Considering the kinetic diameter of a molecule helps in evaluating whether that molecule can enter the pore. Kinetic diameter is the maximum distance between any two points on the molecule.

Acetic acid in aqueous solution has a kinetic diameter of 4.5 \AA (Akbar et al. 2008). The pore size of a zeolite in fresh FCC is greater than 7 \AA , unless the zeolite is ZSM-5 (Venuto and Habib, 1979). There can be increase in pore size in spent FCC because of the disruption of zeolite structure due to Na and other contaminant metals in the feedstock. Coke blocks some of the zeolite pores partially by decreasing the pore size in spent FCC. As there are two significant and opposing effects on pore size, average pore size change is expected to be less. Therefore, acetic acid is expected to enter a majority of the pores.

ZSM-5 has two types of pores. The first type is straight in length and elliptical in cross-section. Their pore size is $5.1 \times 5.6 \text{ \AA}$. The second type of pore is circular in cross-section, arranged in zig-zag fashion. They intersect the straight pores, and their size is $5.4 \times 5.6 \text{ \AA}$. (Sadeghbeigi, R. 2000)

Partial blocking of these pores by coke can affect the entry of acetic acid molecules. However, the intersection of these two types of pores creates supercage cavities of around 9 Å (Sadeghbeigi, R. 2000). Therefore, acetic acid molecules are able to enter the zeolite, when the zeolite is ZSM-5 too.

The percentage of carbon content in spent FCC is around 0.7-1.5 % (Spretz and Sedran 2001). The number of hydrophobic O=Si=O sites in the spent FCC depends upon its Si/Al ratio. Therefore, the properties of spent FCC seem to be affecting the adsorption performance along with the initial concentration of acetic acid used.

Adsorption with Change in pH

As discussed, pH is increased by adding HCl solution, and decreased by adding NaOH solution. When HCl is added, concentration of H^+ increases. H^+ ions have two pathways of interaction in the solution (Akbar et al. 2012).

Pathways:

1. Replacement of Na^+ by H^+ :

Na^+ ions in the zeolite pores are loosely bound, and are readily exchanged with ions in the neighboring aqueous solution (Akbar et al. 2012). Therefore H^+ can replace the Na^+ ions in the zeolite. Akbar et al. (2008) noted that the amount of Na^+ in zeolite is directly proportional to the zeolite's hydrophilic nature as Na^+ have hydration property. Na^+ favors adsorption of water over acetic acid. If the Na^+ are replaced with H^+ , adsorption of acetic acid is favored.

Na content in the spent FCC is not uniform unlike fresh FCC due to the addition of sodium from feed. The source of sodium can be caustic that is added downstream of

the desalter, salts that are carried over by desalter, use of water/steam containing sodium. In fact, the sodium content is typically higher than the content in fresh FCC. (Sadeghbeigi 2000)

2. Formation of O-H bonds:

H^+ can bond with oxygen atoms in alumina tetrahedra and Al-O-Si sites. The OH bond formed attracts polar molecules. Dipole moment of acetic acid and water are 1.74 D and 1.85 D respectively (Akbari et al. 2008). Thus, water is a more polar molecule than acetic acid due to higher dipole moment. Therefore, the OH bond is hydrophilic, favoring adsorption of water over acetic acid.

If replacement of H^+ by Na^+ is more than the formation of O-H bonds, adsorption capacity increases. Otherwise, adsorption capacity decreases. When NaOH is added to increase the pH, OH^- ions react with H^+ to form water. Na^+ ions might replace any H^+ on zeolite. Therefore, adsorption capacity is expected to decrease.

Figures 5.7, 5.8, 5.9, 5.10 depict the effect of pH on adsorption capacity of spent FCC for different concentrations of acetic acid in the solution viz., 15, 25, 40, 55 mg/L.

Fifteen mg/L (Figure 5.7): Initial pH of 15 mg/L of acetic acid solution is 4.2. HCl solution is added to decrease the pH to 4.1. There is slight increase in H^+ ion concentration, of approximately 0.016 mol/L. Additional H^+ ions probably replaced the Na^+ ions present in zeolite, favoring adsorption of acetic acid. Thus, the adsorption capacity might be increasing with decrease in pH in most of the cases. When the pH is decreased to 4.1, the adsorption capacity increased by 2.8 %. This is due to the replacement of Na^+ by H^+ . When pH is decreased to 4.0 from 4.1, the adsorption capacity decreased by 7.4 %. The adsorption capacity is 5.0 % less than the capacity at

pH of 4.2, and is lowest in the data. The formation of O-H bonds and coke distribution with minimal blocking (heterogeneous coke distribution) might be the reasons for the large decrease in capacity. The adsorption capacity increased with change in pH from 4.0 to 3.9 by 14%.

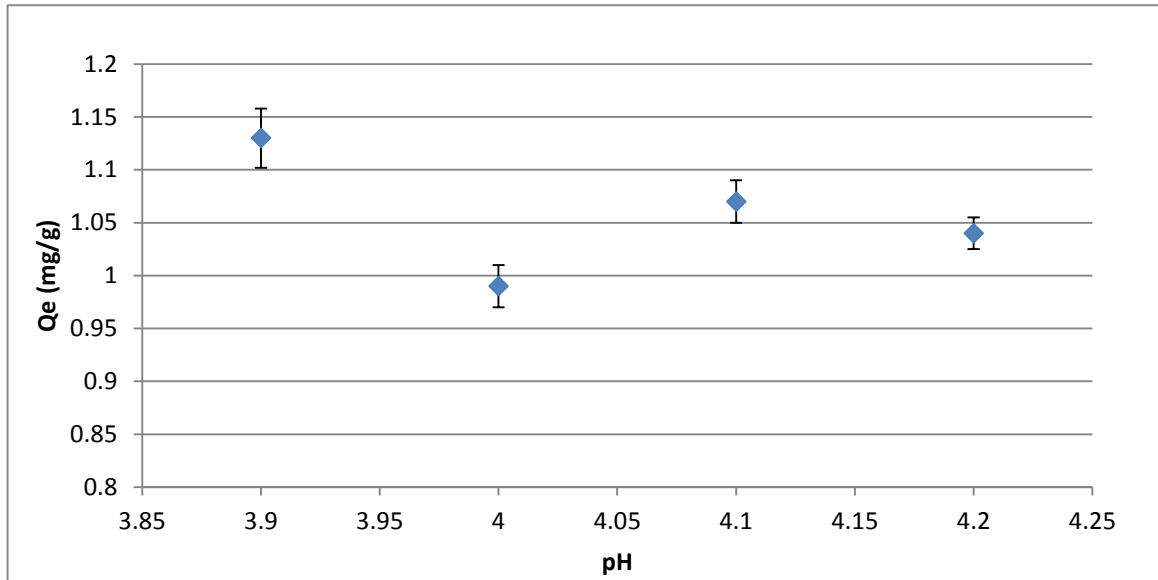


Figure 5.7 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 15 mg/L

Twenty five mg/L (Figure 5.8): Initial pH of 25 mg/L of acetic acid solution is 4.1. The adsorption capacity increased by 5.9 % with decrease in pH to 4.0. The adsorption capacity increased further with decrease in pH to 3.9 by 0.5%. The increase in capacity is due to the replacement of sodium ions by H^+ ions. The pH is increased from 4.1 to 4.2 by adding NaOH solution. The adsorption capacity decreased by 4 %. The decrease is due to the increase in sodium content in the zeolite. The percent change of capacity is high at 15 mg/L, probably because of the low capacity values.

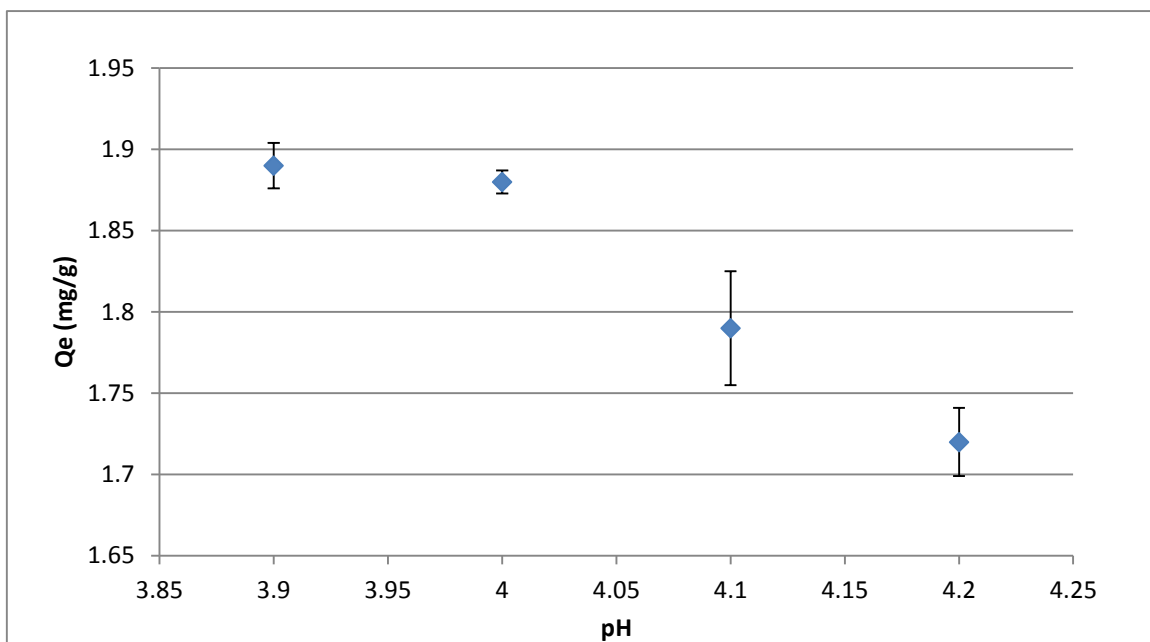


Figure 5.8 Effect of pH on adsorption capacity of spent FCC at initial acetic acid concentration of 25 mg/L.

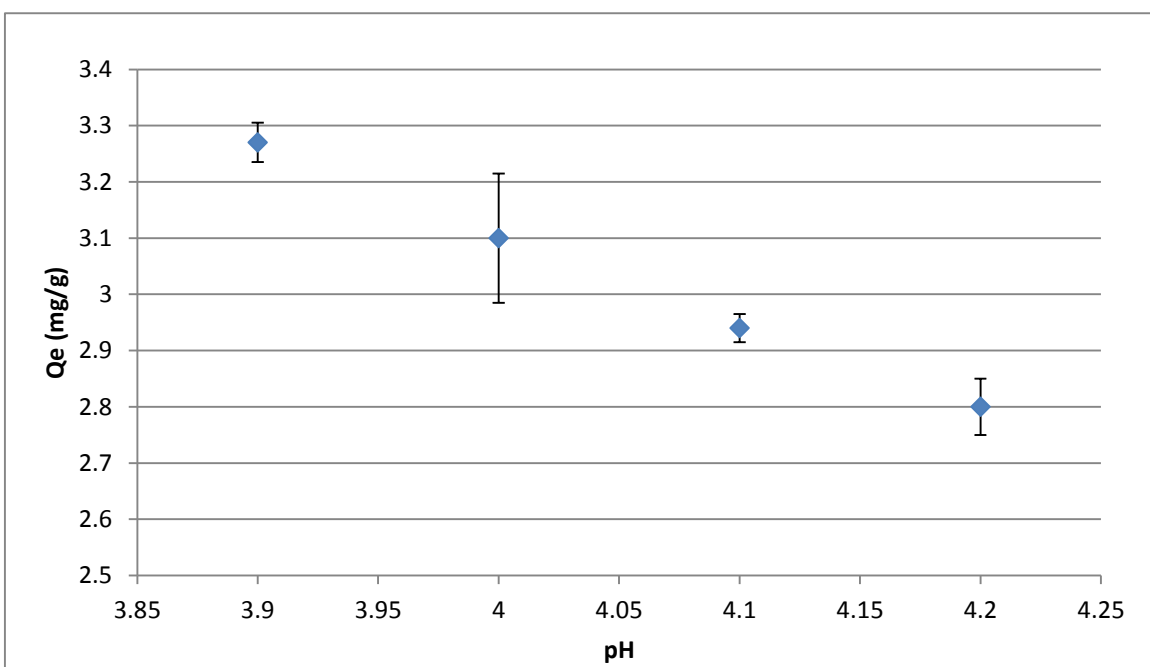


Figure 5.9 Effect of pH on adsorption capacity of spent FCC at 40 mg/L of acetic acid concentration.

Forty mg/L (Figure 5.9): Initial pH of 40 mg/L of acetic acid solution is 4.0. The adsorption capacity increased by 5.5 % with decrease in pH to 3.9. Increase is due to replacement of Na^+ ions by H^+ . The adsorption capacity decreased by 5.1% with increase in pH to 4.1. The adsorption capacity decreased further by 4.7 % with increase in pH from 4.1 to 4.2. Decrease is due to the increase in Na content in zeolite through the NaOH added to increase the pH.

Fifty five mg/L (Figure 5.10): Initial pH of 55 mg/L of acetic acid solution is 3.92. When the pH is increased to 3.99, the adsorption capacity decreased by 3.4 %. This is due to replacement of H^+ by Na^+ in zeolite. The lowest adsorption capacity is observed at pH of 4.09 due to more replacement of Na^+ in zeolite. The adsorption capacity increased with change in pH from 4.09 to 4.21 by 2.6 %. The unexpected increase might be due to the profile of coke (heterogeneous nature) such that the blocking is less in the spent FCC, used for adsorption.

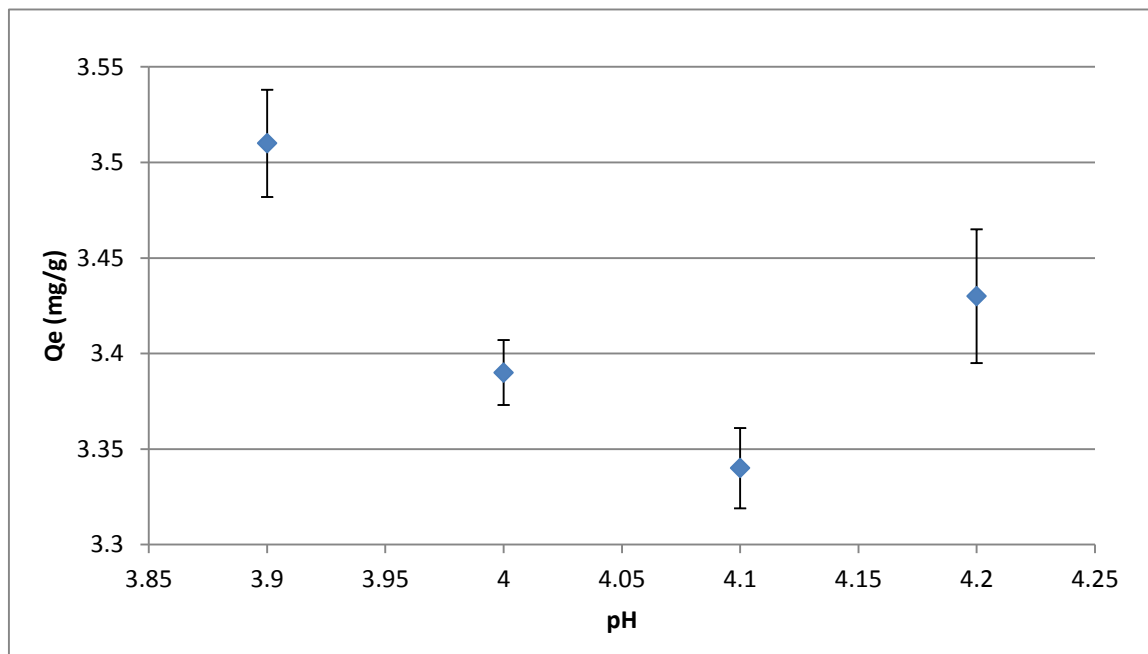


Figure 5.10 Effect of pH on adsorption capacity of spent FCC at 55 mg/L of acetic acid concentration.

Kipling (1948) observed that the adsorption capacity decreased with pH for acetic acid by activated charcoals. In the present work, adsorption capacity decreased with pH at 25 mg/L and 40 mg/L of initial acetic acid concentration. However, adsorption capacity increased with increase in pH at one point each, at 15 mg/L and 55 mg/L concentrations.

As the change in pH is very less, heterogeneous nature of the sample might also have played a role in the adsorption capacity data. The coke distribution and Na content in spent FCC samples is non-uniform. If the coke is formed near the zeolite pore mouths, the pores get blocked, and the adsorption of acetic acid can become difficult, even at low pH.

CHAPTER VI

CONCLUSIONS AND FUTURE STUDY

Conclusions:

The aim of this work is to study the adsorption potential of spent FCC for organics in the hydraulic fracturing flowback. Spent FCC was used to adsorb acetic acid from aqueous solution to acquire batch adsorption equilibrium data. Acetic acid was selected as the target adsorbate as it is the most common organic present in the flowback. The initial concentrations of acetic acid used in the experiments are 15 mg/L, 25 mg/L, 40 mg/L, and 55 mg/L, which are typical for acetic acid in flowback.

Adsorption capacity of spent FCC increased with initial concentration of acetic acid as there are more number of acetic acid molecules available in the solution to get in contact with the same amount of adsorbent. Freundlich isotherm describes the adsorption equilibrium data as the isotherm assumes that the adsorption occurs on heterogeneous surfaces, and coke is heterogeneously distributed in spent FCC. Langmuir isotherm fails

to represent the equilibrium data as the isotherm assumes that adsorption occurs on regular surfaces. The mechanism of adsorption is predominantly through adsorption of undissociated molecules of acetic acid on spent FCC. Coke, Si=O=Si sites of zeolite, and matrix are supposed to be the primary adsorption sites. Acetic acid does not have major problems in entering the pores of the zeolite. At 25 mg/L and 40 mg/L initial acetic acid concentration, adsorption capacity decreased with increase in pH. The increase pH resulted in decrease in H^+ concentration. At low pH, the slightly greater H^+ concentration resulted in the replacement of Na^+ ions in zeolite, making it more hydrophobic. There is one exception each in the above trend of adsorption capacity change with pH, at 15 mg/L and 55 mg/L initial concentrations. The exceptions are present, probably due to the effect of heterogeneous distribution of coke and Na^+ in the spent FCC samples dominating the effect of small change in pH.

Future Study:

Characterization of spent FCC and chemical pre-treatment are the areas in which future work is recommended. Chemical composition data of spent FCC needs to be collected, before using the spent FCC for adsorption. The information on type of zeolite gives the information about the Si/Al ratio and hence, the hydrophobicity. Also, the information on Si/Al ratio and Na content helps in determining the right kind of chemical pre-treatment to increase the adsorption potential. If the Si/Al ratio is low, dealumination with the help of acid treatment is recommended. The concentration of acid for pretreatment has to be determined by testing with different concentrations of acid. High concentration of acid can disrupt the zeolite structure completely. Low concentration will not be effective in increasing the Si/Al ratio.

Experimentation is recommended, using the FCCs with zeolites of different Si/Al ratio. If any of the FCCs yield better or reasonable results for adsorption of acetic acid when compared to the capacity data of banana peels, the FCCs with those zeolites need to be tested for other organics and metals. If the spent FCCs with a chemical pre-treatment yields better results than banana peel waste, the treated spent FCCs need to be tested for the adsorption of other organics. If the spent FCCs do not yield favorable results with a different type of zeolite or chemical pre-treatment, use of spent FCCs as adsorbent is not recommended. The ultimate aim of the work is to evaluate the feasibility of treatment of a high volume waste stream (flowback) with a hazardous waste (spent FCC).

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APPENDIX 1

CALIBRATION

Spectrophotometer has a program (program no. 770) calibrated for volatile acid concentration measurement using the method of Montgomery et al. (1962). However, the calibration is not totally reliable (Hach, 1999). Standard adjust option in the spectrophotometer setup is used to erase the factory calibration in the instrument software, and enter the calibration curve from the present work.

Four standard solutions of acetic acid and water are prepared using quantitative dilution, with the following concentrations: 15 mg/L, 25 mg/L, 40 mg/L, and 55 mg/L. Absorbance of each solution is measured in the spectrophotometer using the analysis method described in the methodology section (Montgomery et al. 1962). A calibration table is created by entering the absorbance values, corresponding to the concentration of the standard solutions. Graph is plotted between concentration of acetic acid and

absorbance of the sample after colorimetric procedure (Figure A1.1).Montgomery et al. (1962) reported that the calibration is linear to at least one percent for the acetic acid. Therefore, linear regression of the graph (Figure A1.1) is done and the best fit line is found out. The best fit line equation is displayed in the Figure A1.1.

Direct coefficient entry of the calibration curve is done in the spectrophotometer (Hach, 1999). First, the linear curve option is selected in the calibration curve. Then the coefficients of the equation are entered.

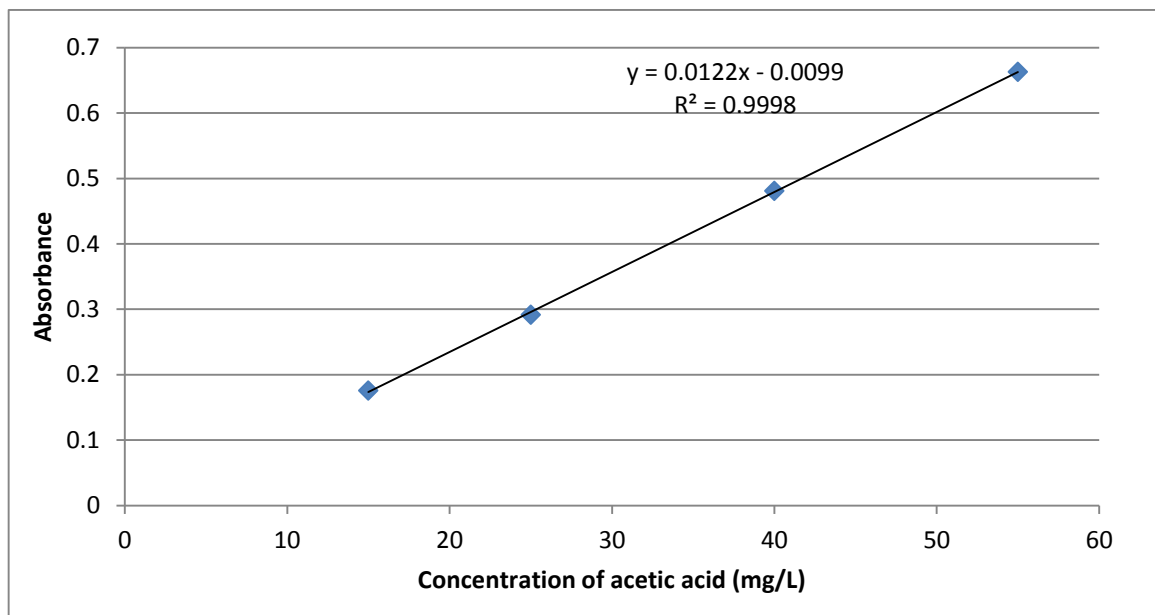


Figure A1.1 Calibration curve

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APPENDIX 2

EXPERIMENTAL TABLES

Adsorption with change in concentration:

Concentration (mg/L)	Adsorption Capacity (mg/g)		
	Run 1	Run 2	Run 3
15	1.12	0.97	1.03
25	1.94	1.77	1.66
40	3.16	2.65	3.49
55	3.71	3.63	3.18

Concentration (mg/L)	Mean Adsorption Capacity (Q_e) (mg/g)	Standard Deviation	Percent Adsorption
15	1.04	0.0755	6.93
25	1.79	0.1411	7.16
40	3.1	0.4232	7.75
55	3.51	0.2857	6.38

Adsorption with change in pH at different concentrations:

15 mg/L

pH	Adsorption Capacity (mg/g)	Percentage Adsorption
4.2	1.04	6.9
4.1	1.07	7.1
4.0	0.99	6.6
3.9	1.13	7.5

25 mg/L

pH	Adsorption Capacity (mg/g)	Percentage Adsorption
4.2	1.72	6.9
4.1	1.79	7.2
4.0	1.88	7.5
3.9	1.89	7.6

40 mg/L

pH	Adsorption Capacity (mg/g)	Percentage Adsorption
4.2	2.80	7.0
4.1	2.94	7.4
4.0	3.10	7.8
3.9	3.27	8.2

55 mg/L

pH	Adsorption Capacity (mg/g)	Percentage Adsorption
4.2	3.43	6.2
4.1	3.34	6.0
4.0	3.39	6.1
3.9	3.51	6.4

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