

# Effect of ferrous mill waste as stabilizer on the arsenic adsorption, microbial removal and strength of clay ceramics

## 5.1 INTRODUCTION

Solid waste accumulation poses a threat to the environment, ecology, and health if it is not collected, managed, and disposed of properly. India alone generates 1, 00,000 metric tons of agro-industrial waste every day. Wooden handicrafts, and the iron and steel sector form the circle of major waste producing industries in India. Reutilization of such wastes is essential to create a sustainable environment. Further, due to the recent industrial revolution, the rampant growth in anthropogenic activities, such as geochemical reactions, mining wastes, and chemical waste disposal, has opened the gateways for the introduction of hazardous heavy metals, such as arsenic, into the aqueous system. WHO lists arsenic among one of ten highly toxic elements. It occurs in abundance in environments from both natural and anthropogenic sources. These long-term geochemical changes cause washout and erosion of arsenic-rich rock soils. [Smedley and Kinniburgh 2002; Li, 2012; Kord, 2013]. Arsenic in an inorganic form in water media is 100 times more toxic than its organic form. Inorganic arsenic represents a threat to the environment and living beings due to its carcinogenic effect over time [Kord, 2013; Hudak, 2010].

The arsenic threat has reached global dimensions because millions of people around the world are heavily dependent on groundwater containing higher concentrations of arsenic than the maximum contaminant level (10 ug/L) recommended by the WHO [WHO, 2008]. Arsenic exposure in drinking water is an important issue in developing countries, where groundwater is generally the preferred drinking source [Fw *et al.*, 1994; Smith *et al.*, 2000]. The elemental state of +3 and +5 form of arsenic commonly occurs in the water systems, depending on the prevailing redox and pH conditions [Tallman and Shaikh, 1980]. This occurrence of arsenic in distinct oxidation states in groundwater and subsurface aquifers has imposed challenges on the development of arsenic removal technology, which can provide safe drinking water to the affected people at low cost, especially to the rural residents of developing countries, such as India.

Literature outlines numerous empirical approaches to separate arsenic from aqueous media [Mohanty, 2017]. The most commonly used treatment techniques for arsenic removal include coagulation, ion exchange, reverse osmosis, electrodialysis, and adsorption. Due to the simplicity of the process as well as its regenerability, the adsorption technology has been widely used to remove toxic heavy metals [Mohan and Pittman, 2007; Ng *et al.*, 2004; Choong *et al.*, 2007]. Removal of heavy metals using organic and inorganic waste as adsorbents has been a good technique because of its low cost, ease of handling and minimal requirement for technology [Babel and Kurniawan, 2003; Zhou and Haynes, 2010; Wang *et al.*, 2003; Mahmoud *et al.*, 2010.]. Various studies have indicated that the inorganic adsorbents and bio-adsorbents are effective in the removal of several heavy metal ions. Some commonly reported inorganic adsorbents are fly ash, fuller earth, red mud, and limestone etc [Diamadopoulos *et al.*, 1993 ; Altundoğan *et al.*, 2000; Pollard *et al.*, 1992; Ohki *et al.*, 1996]. Pollution of water is local. Solutions for preventing this pollution should be local too. This localization of a solution may reduce the costs of transportation of resources and time for achieving it. Rajasthan, Andhra Pradesh, and Tamil Nadu are locations affected by potential anthropogenically influenced arsenic contamination [Kumar and Shah, 2006]. There is a need for the development of efficient, low cost, and environmentally friendly methods to remove heavy metals like arsenic from effluents.

Large surface area materials such as clay become a low-cost choice due to its ease of handling and availability at meagre costs [Kumric *et al.*, 2013; Sdiri *et al.*, 2011; Srinivasan, 2011]. Clay-organic (CO) additive based water filters are considered sustainable drinking water treatment technologies for developing nations [Sobsey *et al.*, 2008]. These units have shown better microbial removal than chemical contaminant removal. In addition, the weak structures of these ceramic units damage these devices during transportation [Yakub *et al.*, 2012, Gupta, S *et al.*, 2018]. Therefore, Gupta *et al.* 2018 initiated localized manufacturing of similar water filters by hereditary potter families in the villages of India and distributing it for use within their village itself. This will reduce the need of transportation and localized manufacturing will sustain potter skills and tradition.

Clay showcases low adsorption properties mainly due to negative charges on its surface. The addition of a certain chemical can enhance their adsorption capacities. Fe containing distinct chemical variants showcase adsorption phenomenon and separate arsenic from aqueous media [Bhowmick *et al.*, 2014; Dousoval *et al.*, 2009; Sigdel *et al.*, 2016]. Availability of Fe based oxides and waste from machining shops is high in developing nation like India. Therefore low-cost development can be sustainable (Te *et al.*, 2018). Te *et al.* 2018 mixed clay, Fe<sub>2</sub>O<sub>3</sub>, Fe powder and rice-based husk taken in a weight ratio to make low-cost ceramics at 600°C. Similarly, clay appended with other metal oxides have been used to separate heavy metallic pollutants [Chen *et al.*, 2010]. Likewise, Bhowmick *et al.* 2014 mixed montmorillonite with zero-valent iron [Bhowmick *et al.*, 2014]. Further, Shafiquzzaman *et al.*, 2013 used iron-based ceramic pellet for arsenic removal [Shafiquzzaman *et al.*, 2013].

Iron and steel manufacturing conglomerates face problems in disposing of machined or scrap iron. The machined or scrap iron can be used to modify filtration ceramics. There have been studies on the reuse of mill waste in the building and construction sector as a replacement for sand in concrete [Li and Wang, 2009; Chen *et al.*, 2011]. Iron powder and iron oxide nanomaterials have been used for wastewater treatment [Xu *et al.*, 2012]. Iron amended biosand filters have been used for decentralized safe drinking water provision [Chiew *et al.*, 2009]. Pottery granules and sand have been coated with iron oxide to remove arsenic [Dong *et al.*, 1996]. However, the mixing of ferrous waste from iron and steel industries as an additive in frustum shaped clay ceramic water filter system for arsenic removal remains unexplored [Gupta *et al.*, 2018].

This study jointly addresses the three major issues,

- a) solid (industrial) waste management,
- b) low-cost arsenic removal material and
- c) improving structural integrity of clay ceramics used to filter drinking water.

Ferrous mill waste from local machining shops in Basni Industrial area, Jodhpur, Western Rajasthan, have been used as stabilizers to the clay-organic residue immingles to develop modified ceramics. These ceramic materials were investigated for As(V) removal in term of adsorption kinetics, time and pH change. In this study, microbial removal and strength of the ferrous additive based clay ceramics (FCC) were also compared with clay ceramics (CC) without ferrous waste addition.

## 5.2 MATERIALS AND METHODS

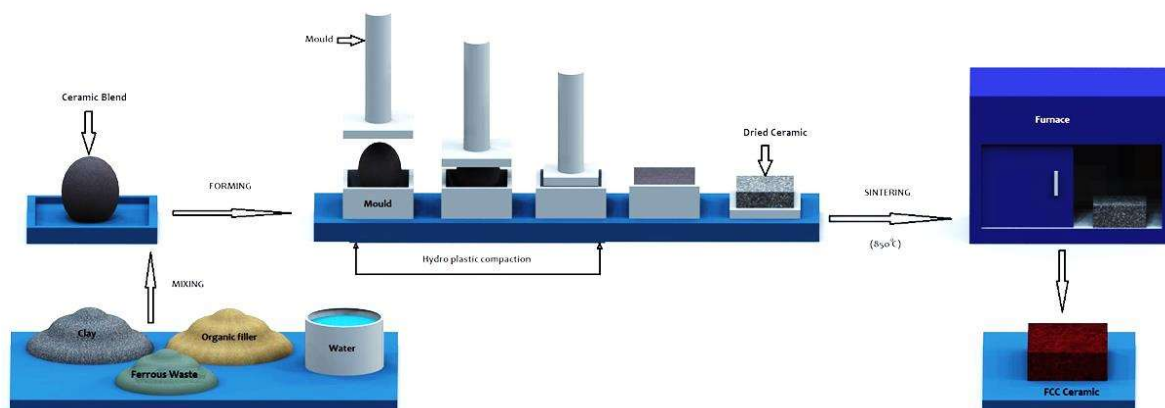
### 5.2.1 Materials and Chemical Reagents

As a matrix material, the clay was collected from the Barmer district in the Mokalsar village of Siwana tehsil, Rajasthan. The clay received was first plunged in deionized water to remove larger particles and debris, and dried at 104± 1 °C for 24 hours. The dried clay was wedged thoroughly by pounding with a wooden mallet. The crushed clay was passed through a 0.5 mm

sieve (ASTM 35 mesh size). Carpentry residue was used as organic pore former. It was freely available and collected from a local wooden handicraft shop (Timber mart Jalori Gate) in Jodhpur Rajasthan and sieved through a 1-mm sieve (ASTM 18 mesh size). The ferrous powder was obtained from a Vishwakarma fabricator, Basni Industrial area, Jodhpur. The ferrous mill powder was sieved through .074 mm (ASTM 200 mesh size). As (V) stock solution (100 mg/L) was prepared by dissolving the appropriate amount of  $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ . NaOH (A6756, Merck) and HCl were used for solution pH adjustment.

### 5.2.2 Adsorbent development

The porous ceramic adsorbent (FCC) was developed by mixing clay soil, sawdust, and ferrous mill powder homogeneously at a ratio of 45: 45 :10 on a volume fraction basis (**Figure 5-2**). The powders were manually mixed with the addition of deionized water to form a uniform wet blend. The wet paste was compacted into two different sizes: one in the form of small square pellets of  $15 \times 15 \text{ mm}^2$  for the batch adsorption test. The second was  $100 \times 100 \times 15 \text{ mm}^3$  dimensions for performing the mechanical strength test. Oiling the mould is done before filling the wet clay-ferrous paste into the mould. The mixture is filled into the mould and pressed into a square form using a 50-ton compaction machine (Model HBPO10, KEN-985-5000K, UK). The samples were kept for drying at ambient temperature conditions for a period of one week, and were then sintered at  $850^\circ\text{C}$  in an electric furnace (TEXCARETM Muffle Furnace 220V,  $250 \times 340 \times 180 \text{ mm}^3$  (w  $\times$  d  $\times$  h) for 2 hours to carbonize and produce pores. The square samples were cut using a ceramic cutter (Bosch GDC 120) to assess the strength of samples.



**Figure 5-1 :** Manufacturing of Ferrous mill mixed clay Ceramics

### 5.2.3 Batch mode adsorption study

Batch mode experiments were carried out at room temperature ( $25 \pm 1^\circ\text{C}$ ) in a 100-mL teflon bottle. They were shaken at 80 rpm for a desired duration. For kinetic studies, 1 mg/L of arsenic (V) solution ( $\text{pH} = 6.5 \pm 1^\circ\text{C}$ ) was used and kept in contact with 5 g of FCC adsorbent for the desired period of 5, 10, 15, 30, 45, 60, 75, and 90 mins. The effect of pH from 3 to 11 was studied and the desired pH was adjusted by adding HCl or NaOH. Isotherm experiments were performed with As (V) concentration of 50, 100, 500 and 2,000  $\mu\text{g/L}$  for an adsorbate dose of 1 g. Freundlich and Langmuir model isotherms were studied to evaluate the adsorption capacity and describe the arsenic's removal onto solid ceramics. The filtrate concentration was analyzed within 24 hours. All the experiments were carried out in triplicate to ensure reproducibility. The same parameters were applied for CC ceramics testings.

#### 5.2.4 Microbial Removal Study

To check the microbial removal efficiency of ceramic wares, microbial removal test was carried out at Biological Engineering Department at I.I.T Jodhpur, Jodhpur, Rajasthan, where cultures of the non-pathogenic *Escherichia coli* DH10B™ strain were grown in Miller's LB Broth at 37° C for 24 hours with aeration by stirring at hotplate. Microbial removal test was carried out until 500 mL of solution passed through the FCC and CC filters prepared on a laboratory scale. The effluent was stored in 125 mL increments three times during each test. Two blanks were made for each set of controls. The E.Coli in water was enumerated as per the procedure mentioned in Standard methods for the Examination of Water and Wastewater [American Public Health Association (APHA)]

### 5.3 MATERIAL CHARACTERIZATION

#### 5.3.1 Composition analysis

X-ray fluorescence technique was used to decipher the chemical compounds present within the Fe based stabilizer and FCC ceramics. The Fe waste and ferrous based clay ceramics were separately powdered using agate mortar and pestle. Powdered sample (2 mg) were analysed in a Bruker S4 Pioneer facility (X-ray fluorescence instrument at JNU New Delhi) to determine their chemical compositions.

#### 5.3.2 Mineralogy determination

The mineralogical investigation of ferrous waste and the ceramic sample was carried out in a Bruker D8 ADVANCE diffractometer (at I.I.T. Jodhpur) using filtered copper K $\alpha$  radiations [Cu-K $\alpha$  radiation,  $\lambda = 1.5418$  nm] with a step size of 0.02 and scan speed of 0.5.

#### 5.3.3 Surface Morphology

The microstructural evolution of CC and FCC ceramic pellets before and after arsenic treatment was assessed using scanning electron microscopy (FEI, Quanta 200, MNIT Jaipur). Gold-coated ceramics were placed in the SEM chamber for imaging analysis. The percentage porosity and pore size information was determined using mercury intrusion porosimetry.

#### 5.3.4 Atomic absorption spectroscopy

As (V) concentration prior and post adsorption was measured by Atomic absorption spectroscopy (AA500, MRC, MNIT Jaipur, Jaipur, India). The pH studies were performed using pocket-sized pH meter (Oakton pHTestr 30 Waterproof Pocket Tester). Fourier transform infrared spectroscopy (Bruker™ Vertex,70V, Germany) was used to analyze the chemical profile of ceramics before and after arsenic treatment.

### 5.4 MECHANICAL CHARACTERIZATION

#### 5.4.1 Flexural Strength test

The flexural strength test was carried out on a laboratory-based Universal testing machine (Model EZ-50, Lloyd Instruments, Germany). The ceramics specimens of 75 mm  $\times$  15 mm  $\times$  15 mm size were processed with the three-point bend test set up at a loading rate of 0.1 Ns<sup>-1</sup> [Plappally *et al.*, 2011]. The results of flexural strengths were recorded using Nexygen material testing software (Nexygen plus 01/3366, Lloyd Instruments, Germany).

#### 5.4.2 Compression strength test

For the compressive strength test, ceramic specimens of 35 mm  $\times$  15 mm  $\times$  15 mm cross-section were cut (Bosch GDC 120). A loading rate of 0.1 N/s was applied along the 35-mm axis until the sample was completely crushed [Plappally *et al.*, 2011]. Compressive strength data were recorded digitally using Nexygen plus material testing software.

## 5.5 RESULTS AND DISCUSSION

### 5.5.1 Properties of ferrous waste and ceramic adsorbent

Table 5-1 shows the chemical composition of ferrous waste. The waste contained high percentage of iron oxide and silica.

Table 5-1: Chemical composition (Wt %) of porous ceramic adsorbent

Weight Percentage	Ferrous Waste
Fe <sub>2</sub> O <sub>3</sub>	55.545
SiO <sub>2</sub>	9.552
Al <sub>2</sub> O <sub>3</sub>	1.874
CaO	0.482
MnO	0.444
LOI	32.103

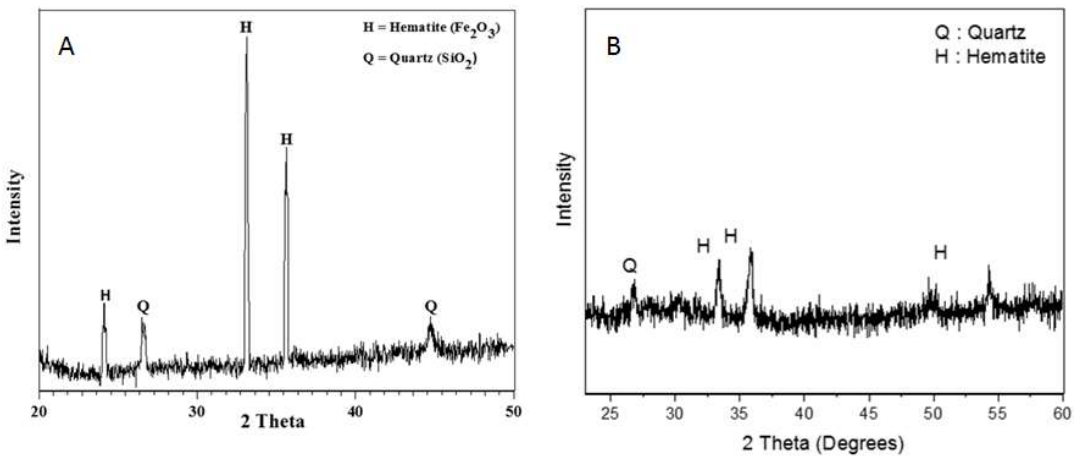
FCC (in Table 5-2) showcases dominance of silica and oxides of iron (constituting ~ >80% weight percentage). The quantity of ferrous oxide within FCC is much more than compared to that of CC in Figure 4-4.

Table 5-2: Chemical composition (Wt %) of porous ceramic adsorbent

Weight Percentage	FCC
Fe <sub>2</sub> O <sub>3</sub>	34.642
SiO <sub>2</sub>	48.574
Al <sub>2</sub> O <sub>3</sub>	9.959
CaO	2.386
MnO	0.895
MgO	1.681
K <sub>2</sub> O	1.502
TiO <sub>2</sub>	0.361

The MIP data displayed an average porosity of 42.24 % and mean pore diameter between 1-5µm, suggesting that the adsorbent is microporous according to pore classification of the International Union of pure and applied chemistry [Kuila *et.al*, 2013].

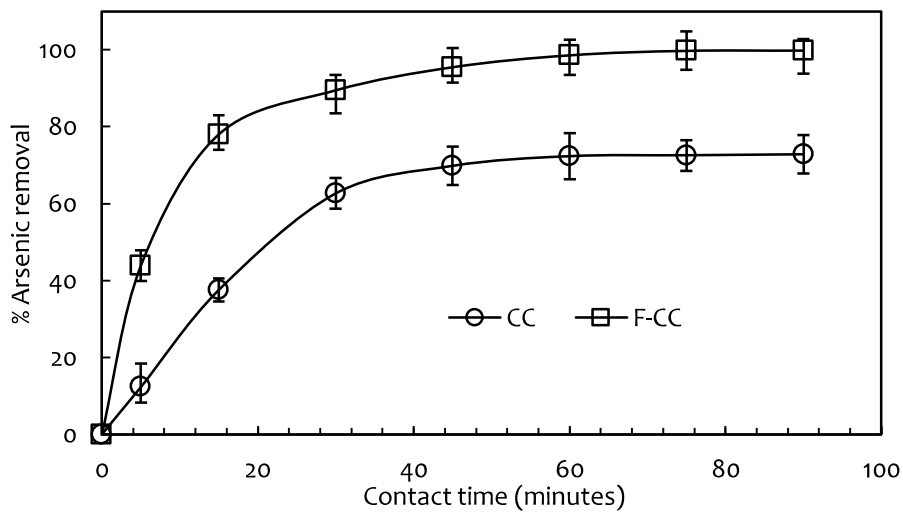
Figure 5-2 shows the XRD pattern of the ferrous waste and porous ceramic adsorbent. The mill waste contained hematite as the dominant phase along with small amount of quartz. The sintered ceramic possessed main crystalline phases of quartz and hematite which were contributed by clay and iron oxide, respectively.



**Figure 5-2 :** XRD pattern of ferrous mill waste and ferrous mixed porous ceramic adsorbent

### 5.5.2 Effect of contact time

The effect of contact time of contaminated water with the FCC is premeditated during batch adsorption studies. The effect of residence time on As (V) removal was shown in **Figure 5-3**. The curve showcases a high As removal gradient during the initial 20 min of contact and then peters slowly. An asymptote or saturation is reached with an hour. This behaviour suggests the reduction in the amount of vacant surface sites with time. Based on these results, ninety minutes was taken as the time for adsorption experiments to reach equilibrium. With increase in contact time, the existence of repulsive forces between solute molecules in the aqueous solution and solid phase causes difficulty in filling the vacant surface sites is characterized by layer formation which secludes other active surface sites as well [Manning *et al.*, 2002; Fendorf *et al.*, .2002, Yao *et al.*, 2014]. This also means that FCCs can be used to achieve large removals within a short time interval. The addition of iron into the clay mixture has enhanced the arsenic removal efficiency.



**Figure 5-3 :** Effect of contact time on the sorption capacity of As (V) ions onto FCC and CC ceramics

### 5.5.3 Pseudo Second order empirical model

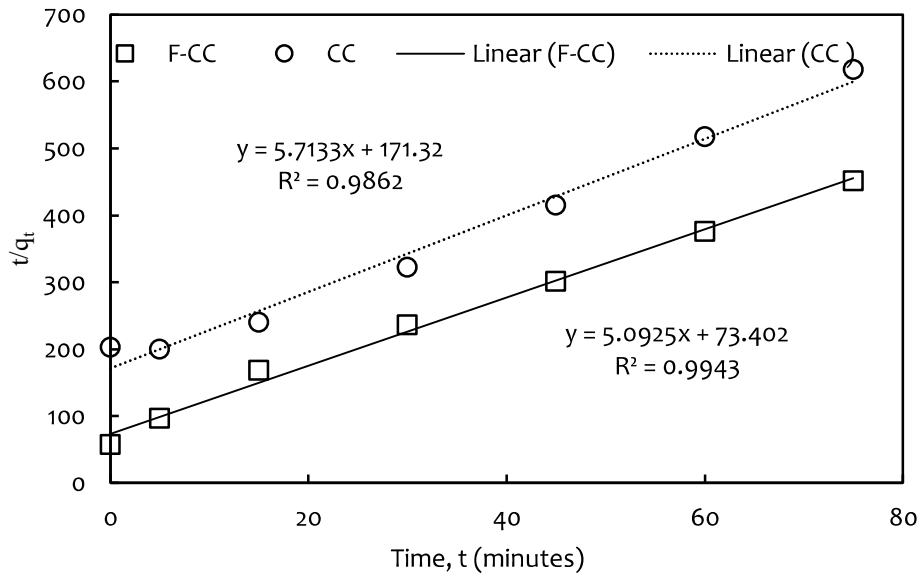
A pseudo second-order empirical model was used to retrodict the rate of As (V) adsorption [Salameh *et al.*, 2010]. Here  $t/q_t$  was plotted against time  $t$  [Far *et al.*, 2012; Salameh *et al.*, 2010] (see fig. B). The following Eq.s Eq. 5.1, Eq. 5.2 and Eq. 5.1 will help model other parameters and constants [Far *et al.*, 2012; Salameh *et al.*, 2010].

$$t/q_t = 1/kq_e^2 + t/q_e \quad (5.1)$$

$$q_t = Kq_e^2t / 1 + Kq_e t \quad (5.2)$$

$$h = kq_e^2 \quad (5.3)$$

The table below enumerated the related values of constants and other parameters defined Eq.5.1, Eq.5.2 and Eq. 5.3 (**Table 5-3**)



**Figure 5-4 :** Pseudo second-order plot of FCC and CC ceramics

The correlation coefficient ( $R^2$ ) of the pseudo second-order model for FCC was closer to .99 The tabulation and the plots predict a possible chemisorption reaction on the FCC surfaces [Qi *et al.*, 2015]. From the pseudo second order model, the initial adsorption rate ( $h$ ) calculated by  $h = kq_e^2$  for As (V) are shown in **Table 5-3**

**Table 5-3 :** The parameters obtained from fitting the sorption data of As (V) onto various porous ceramics using pseudo-second order Eq. (Eq. 2).  $h = kq_e^2$  and  $R$  is the regression coefficient for the linear plot.

Sample	$q_e$ (mg/g)	$K$ (g/mg min)	$h$ (mg/g min)	$R^2$
CC	0.175030193	0.190531152	0.00583703	0.9862
FCC	0.196367207	0.353308578	0.013623607	0.9943

The adsorption capacity obtained using FCC was higher than that obtained using clay - organic residue (CC) ceramics. The addition of ferrous waste into the clay-organic waste matrix had increased the amount of iron into the (FCC) membranes. Adsorption of arsenic may have enhanced due to positive charges on FCC surface [Bowell, R. J., 1994].

### 5.5.4 Effect on surface morphology

Figure 5-5 shows the FCC surface characteristics prior to and after arsenic adsorption for a time period of ninety minutes. Addition of ferrous waste has resulted in dense morphology of the FCC ceramic.

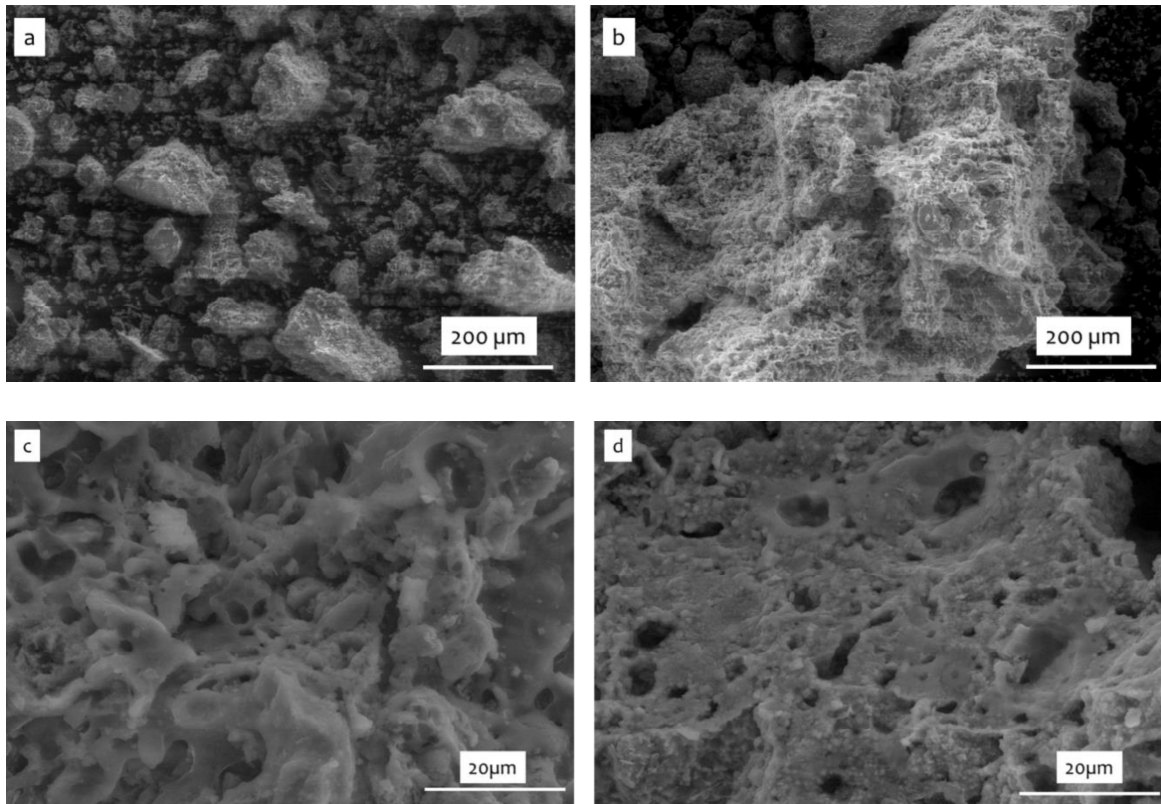
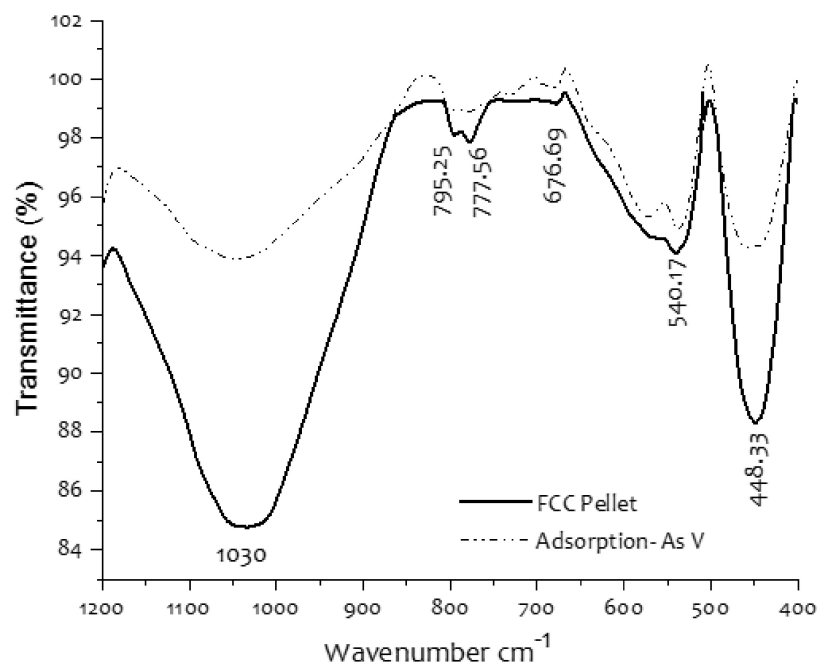


Figure 5-5 : Comparison between surface morphology of ceramics before arsenic treatment a) CC & b) FCC and after treatment, c) CC and d) FCC at 500x

FCC in (Figure 5-5 b) had numerous pores prior to contact with arsenic contaminated water. After As (V) adsorption the surface in Figure 5-5 d showcases smoother surface with layers (similar to solidified lava flows) covering the pores. Binding between arsenic and iron by forming large complexes on the surfaces of FCC is envisaged as observed using FTIR analysis.

The arsenic adsorption in the FCC ceramic sample was assessed using FTIR analysis.





**Figure 5-6 :** FTIR spectrum of ferrous ceramic before and after As (V) adsorption

The FTIR spectra of the FCC adsorbent prior and post As (V) adsorption is shown in **Figure 5-6**. The bands at 1030  $\text{cm}^{-1}$  and 795.25  $\text{cm}^{-1}$  indicated stretching vibration of Si-O-Si group and Si-O deformation [Nayak and Singh, 2007; Petala *et al.*, 2013; Tandon *et al.*, 2013]. The peak observed 676.69  $\text{cm}^{-1}$  denoted the spectrum for iron oxide ( $\text{Fe}_2\text{O}_3$ ) [Lt *et al.*, 2010]. The peak bands at 540.17  $\text{cm}^{-1}$  and 448.33  $\text{cm}^{-1}$  resembled with that of Si-O-Al and Fe-O groups, respectively [Chen *et al.*, 2011; Li *et al.*, 2016]. After As (V) adsorption, the IR spectra displayed an increased percentage transmittance with reduction of stretching of peak bands of corresponding bands. No presence of new peak bands was observed. This could be due to As (V) adsorption on the surface of the FCC adsorbent.

### 5.5.5 Effect of pH

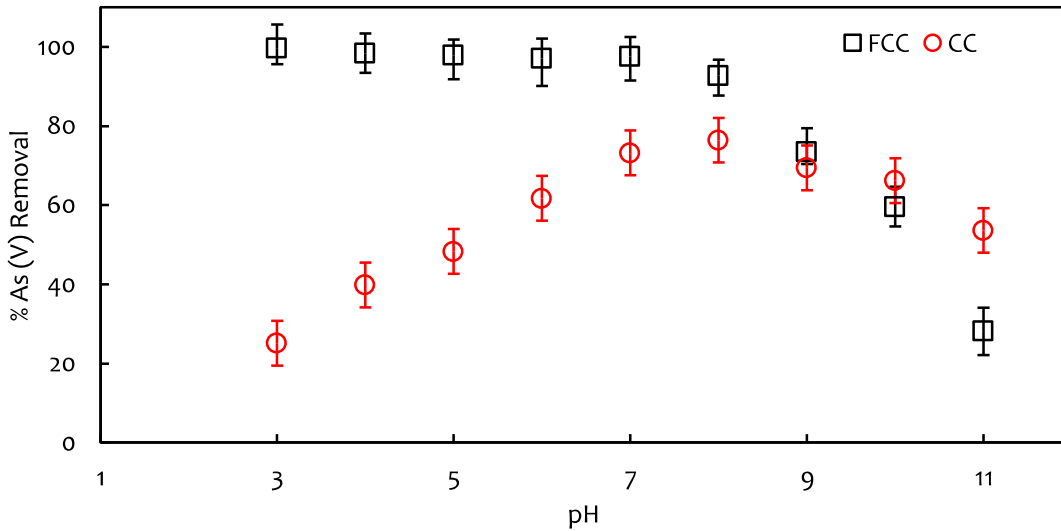
From **Figure 5-7** it is observed that As (V) removal using FCC favoured the acidic aqueous environments. FCC enumerated no significant change in adsorption over the pH range from 3 to 7. The removal attenuated above pH of 9. According to Cheng *et al.* 2010, As in aqueous media exists in distinct states. These states are discussed in the following table.

Chemical transformation of As in water with varying pH [Cheng *et al.*, 2010] is displayed below :

**Table 5-4 :** Transformation of As (V) in water [Source: Cheng *et al.*, 2010]

pH of Aqueous Solution	Form of As (V)
<2.2	$\text{H}_3\text{AsO}_4$
2.2-6.98	$\text{H}_2\text{AsO}_4^-$
6.89-11.5	$\text{HAsO}_4^{2-}$
>11.5	$\text{AsO}_4^{3-}$

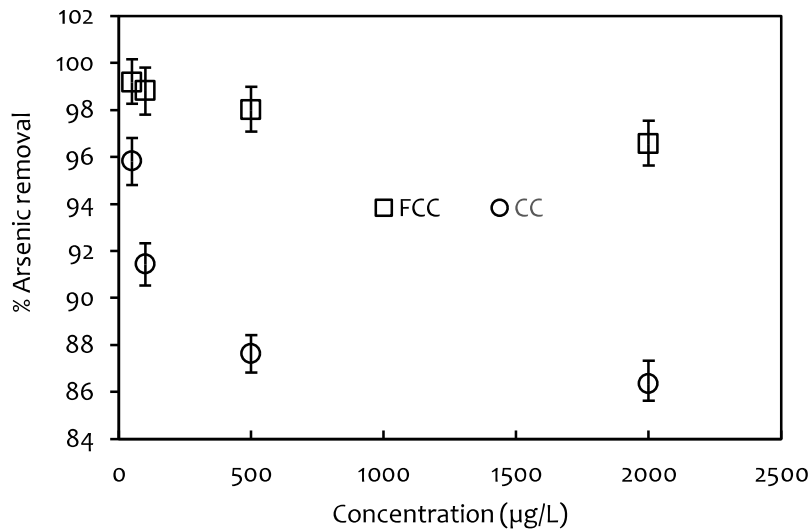
Following the theory provided in the **Table 5-4**, the plot in **Figure 5-7** illustrates that FCC was more positively charged during a pH range of 3 to 7 which confirms electrostatic attraction between As and FCC surface (Cheng *et al.*, 2010). The abrupt decrement in the removal efficiency beyond pH of 9 symbolizes electrostatic repulsion between the As (V) and FCC ceramic. The change in pH influences the FCC surface charge which impacts surface based adsorption kinetics [Cheng *et al.*, 2010].



**Figure 5-7 :** Effect of pH on arsenic removal efficiency

### 5.5.6 Effect of initial concentration

High arsenic removal is showcased at low concentration of arsenic in aqueous media from (**Figure 5-8**) [Zeng *et al.*, 2007]. FCC ceramics displayed higher arsenic removal in comparison with CC at higher arsenic concentrations. The percentage of arsenic rejection decreased with increasing initial concentration. The result attests that large surface area to concentration ratio value showcases high As removal [Wilkie and Hering, 1996]. The clay ceramic and ferrous additive in FCC jointly provided the more active surface of contact which promoted greater adsorption of metal ions at lower concentrations.



**Figure 5-8 :** Effect of adsorbate concentration on arsenic adsorption of FCC and CC ceramics

### 5.5.7 Adsorption Isotherms

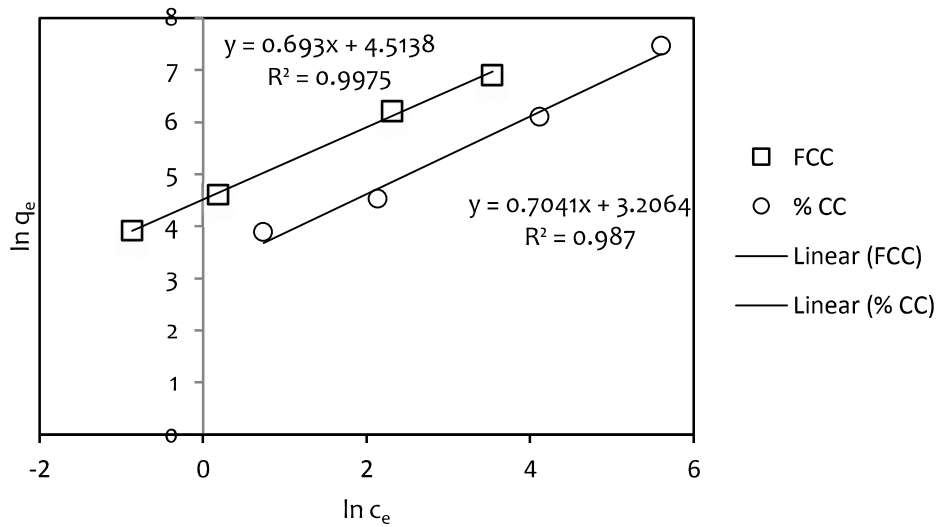
The adsorption isotherm indicates the distribution of As contaminant in the liquid and the solid phase with adsorption phenomenon inching to equilibrium. Langmuir and Freundlich isotherm equations are widely used models to describe this distribution. As (V) adsorption isotherms obtained from FCC and CC treatments and are shown in **Figure 5-9** and **Figure 5-10**. These isotherms represent the adsorption behavior of As(V) on the different adsorbents as a function of increasing aqueous As(V) concentration for a contact time of 1 h.

#### Freundlich Isotherm

The Freundlich mathematical model deals with physicochemical adsorption on heterogeneous adsorbent surfaces. This assumption suggests that there are different active sites on the adsorbent surface. The isotherm model was used to analyze the result of As(V) adsorption on FCC and CC as adsorbents (**Figure 5-9**) [Chassapis *et al.*, 2010]. The Freundlich mathematical expression can be expressed by the Eq. (5.4).

$$\ln q_e = \ln k_f + (1/n) \ln C_e \quad (5.4)$$

where  $k_f$  and  $n$  are constants related to the adsorption capacity and affinity, respectively. The constants can be determined as the intercept and slope of a plot of  $\ln q_e$  versus  $\ln C_e$ . The value of  $k_f$  and  $n$  for the ceramics are tabulated in **Table 5-5** [Chassapis *et al.*, 2010]. The characteristic of the adsorption can be investigated using value of  $n$  and  $k_f$  indicates the sorption capacity of the adsorbent. The adsorption is said to be favourable when  $n$  has a value between 1 and 10 [Fufa *et al.*, 2014, Chen *et al.*, 2012]. In this present case of FCC, value for  $n$  for As (V) was 1.444, which indicated favourable adsorption. The sorption capacity of adsorbent ( $k_f$ ) after addition of ferrous waste has increased ~3.6 times in comparison with CC ceramics. The linear plot between  $\ln q_e$  versus  $\ln C_e$  showed that adsorption data fitted well with a high coefficient of determination of 0.9975 for FCC adsorbent.



**Figure 5-9 :** Freundlich Isotherm plot of FCC and CC

**Table 5-5 :** The parameters obtained from fitting the sorption data of As (V) onto various porous ceramics using Freundlich Eq. (Eq. 5.4) and R is the regression coefficient for the linear plot.

Parameters	FCC	CC
n	1.444	1.4202
$K_f$ [ $\mu\text{g/g (L}/\mu\text{g)}^{1/n}$ ]	91.16763913	24.68504
$R^2$	0.9975	.987

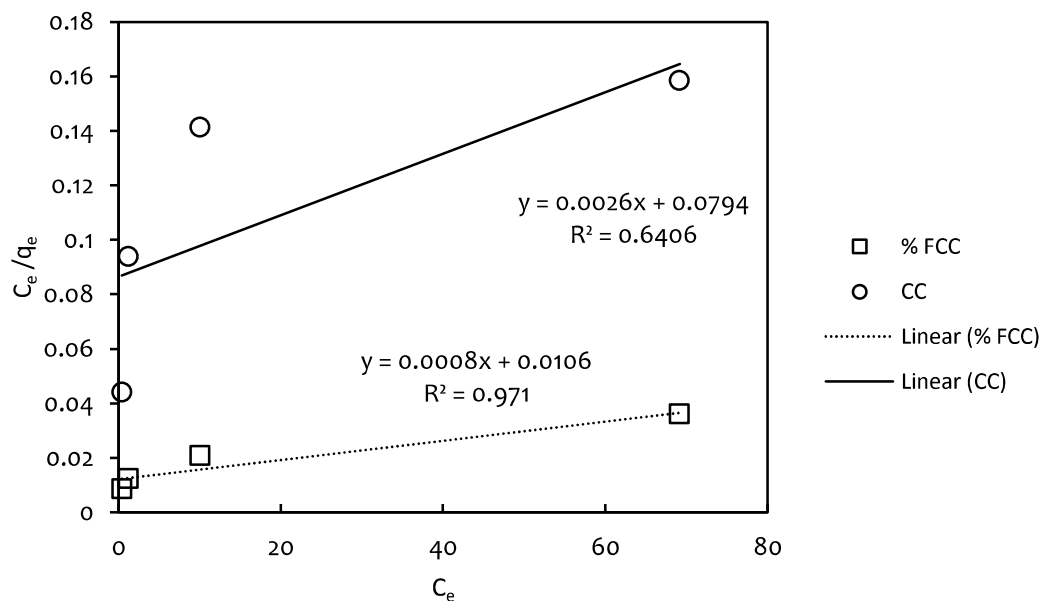
### Langmuir Isotherm

The langmuir model was applied to find the maximum arsenic uptake ( $q_{\max}$ ) at different arsenic (V) concentrations. The linear form of Langmuir Eq. at a given temperature is represented by [Liu *et al.*, 2005]:

$$C_e/q_e = 1/bq_{\max} + (1/q_{\max})C_e \quad (5.5)$$

where  $C_e$  is the ionic concentration of arsenic ( $\mu\text{g/L}$ ),  $q_{\max}$  is the maximum amount of As(V) adsorbed onto 1 gm of the adsorbent ( $\mu\text{g/g}$ ),  $b$  is the adsorption constant ( $\text{L}/\mu\text{g}$ ) related to the affinity of the binding sites. The Langmuir Eq. is based on the monolayer sorption onto a homogeneous surface [Liu *et al.*, 2005].

The linear plot of  $C_e/q_e$  versus  $C_e$  (**Figure 5-10**) displayed that the adsorption in FCC ceramics obeyed langmuir isotherm model with a greater coefficient of determination of 0.971 as compared to CC ceramics. The higher  $R^2$  value for FCC indicates monolayer adsorption of As (V) onto FCC adsorbent. The isotherm parameters  $q_{\max}$  and  $b$  were calculated from the slope and intercept of the plot (**Figure 5-10**) and listed in **Table 5-6**. It could be seen that both  $q_{\max}$  and  $b$  remain higher for As(V) adsorption onto ferrous waste mixed clay ceramics as compared to clay ceramics without ferrous waste.



**Figure 5-10 :** Langmuir isotherm for FCC and CC ceramics

**Table 5-6 :** The parameters obtained from fitting the sorption data of As (V) onto various porous ceramics using Langmuir Eq. (5.5) and R is the regression coefficient for the linear plot.

Parameters	FCC	CC
$q_{max}$ ( $\mu\text{g/g}$ )	1250	384.6153846
$b$ ( $\text{L}/\mu\text{g}$ )	0.075471698	0.032745592
$R^2$	0.971	.6406

The obtained results from both the Freundlich and Langmuir isotherms suggest that the adsorption equilibrium data fitted very well to both the empirical models.

### 5.5.8 Microbial Removal

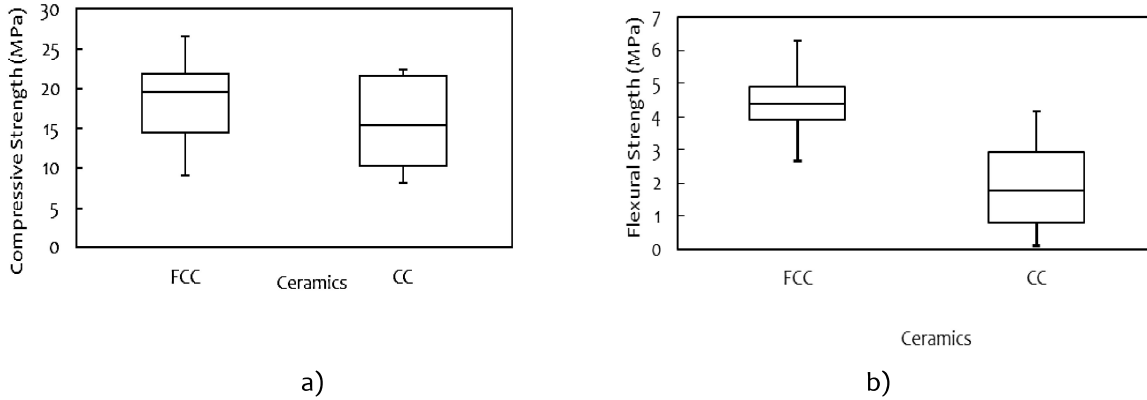
The percentage of *E.Coli* removed by ceramics with and without the addition of ferrous waste is shown in **Table 5-7**. There was a slight increase in the log removal rate due to the addition of ferrous material. Likewise, Brown and Sobsey (2009) have used iron compounds to enhance virus removal in a clay mixture [Brown and Sobsey, 2009]. High *E.coli* removal efficiency was observed in both FCC and CC ceramics.

**Table 5-7 :** *E.coli* removal data from FCC and CC ceramics

Ceramic Wares	Log Reduction Value (LRV) $= \log_{10} I/F$	Efficiency of <i>E.coli</i> Filtration ( $1-F/I$ )
FCC	2.90309	.998
CC	2.823909	.993

### 5.5.9 Mechanical characterization

The compressive and flexural strength of the clay ceramics experienced an uplift with the addition of ferrous powdered waste (**Figure 5-11**). Addition of ferrous waste reduced the porosity and surface roughness of the ceramics and made the structure denser (**Figure 5-11 a** and **Figure 5-11 b**). The plots show that addition of ferrous element increases average flexural strength ~ 2 times and compressive strength increases ~1.33 times the ceramics without ferrous waste.



**Figure 5-11 :** Comparison of a) compressive and b) flexural strength behaviour of ceramics with and without addition of ferrous waste

## 5.6 CONCLUSION

The composition of porous clay ceramics which form the media for rural household water filtration was modified to improve upon their arsenic removal efficiency and mechanical sustenance. The fluorescence and mineralogy study showed the emergence of hematite and quartz as the prominent phase. The addition of ferrous mill waste to the clay-saw dust composition worked as a pore blocker making the ceramic structure denser in the structure. In the batch adsorption study, 90 minutes contact period gave high arsenic removal efficiency of ~99% and beyond that time no remarkable removal occurred. This indicated that the adsorption capacity of the clay ceramics enhanced with the addition of ferrous waste. The adsorption kinetics followed the pseudo-second-order model. The surface of ceramics after arsenic treatment (for a period of 90 mins) became smooth and contained small pores. The isotherm study indicated that the porous ceramics fitted well with the Freundlich and Langmuir models. High microbial removal efficiency was shown by FCC ceramics. The mechanical sustenance of the ferrous mixed ceramics showed increment in comparison with ceramics having no ferrous additive.