6

Effect of marble slurry as waste additive on the arsenic adsorption, microbial removal and strength of porous ceramics

6.1 INTRODUCTION

India is among the top five countries of the world that dominates the marble production. And Rajasthan is the richest marble producing state, producing 90% of India's marble [Rassin, 2012; Tozsin, 2014; Singh and Rajoria, 1987]. It's been reported that there are around 1100 marble processing units all over the Rajasthan where mined marble blocks undergo various operations such as cutting, polishing, machining and dressing which produces nearly 5-6 million metric tons of slurry per year. Improper collection and open dumping of fine slurry (<45-300µm size), results in heaps of rarely degradable wastes imposing adverse effects on ecology, human health and air quality. The unsystematic disposable practices of marble sludge has raised huge environmental problems in several ways such as making topsoil non porous and impermeable, polluting drinking water resources and deteriorating ground and surface water quality [Central Pollution Control Board Zonal Office (Central), 2011-12, Technology and Action For Rural Advancement (TARA), New Delhi]. Thus, reutilization of such industrial wastes is essential to create a sustainable environment.

Groundwater is a critical local resource. India is the largest user of groundwater for drinking and other domestic purposes [Saha, 2018]. In the last several decades development in India occurred in an uncontrolled way and anthropogenic activities spilled across safe zones. Unabated mining and chemical waste disposal like arsenic into the aqueous system are rampant with development and growth at different locations in India. The occurrence of arsenic in distinct oxidation states in groundwater and subsurface aquifers has enforced challenge on developing low-cost systems for efficient arsenic removal, especially for rural parts of developing countries [Abhinav et al., 2016].

Rural India severely suffers from arsenic-laced water, which has widely prevailed cases of skin lesions and skin cancer. The lack of effective and inexpensive solutions for treating arsenic - contaminated drinking water for low-income families may be one of the prominent reasons for such scenario [Ghosh and Singh, 2009 ; Bandyopadhyay, 2016].

Over the course of time, many technologies like adsorption, ion exchange, precipitation-coagulation and membrane separation have been developed, out of which adsorption has emerged as a widely investigated technique for arsenic removal from water. Adsorption has received increased attention due to its inexpensive, easy and efficient operation [Choong et al., 2007 ; Bissen and Frimmel, 2003]. Clay and clay minerals have been used as cost-effective and efficient adsorbents for arsenic removal from water [Mohan and Pittman, 2007; Zeng and Jiang ,2005 ; Goldberg, 2002]. Also, clay-based ceramic water filters developed for low- income families have shown potential for removal of pathogenic and chemical contaminants from drinking water [Archer et al., 2011; Kumar, 2011 ; Brown and Sobsey, 2010]. However, the low adsorption capacity of clays has encouraged the addition of additives to enhance the sorption potential of clays [Yakub and Soboyejo, 2013]. Further, the fragility of clay ceramics has led to difficulty in their transportation and reduction of lifespan [Plappally, 2010; Yakub, 2012].

Various initiatives to address the two major issues documented above i.e. sustainable industrial waste reutilization and development of low-cost system to provide contaminant-free drinking water to rural families have been reported in the literature where soil, carbonaceous matter and industrial by-products have been utilized in wastewater treatment as an adsorbent

materials to remove distinct heavy metal contaminants from aqueous solution [Choong *et al.*, 2007; Maji *et al.*, 2008; Agrafioti *et al.*, 2014; Sud *et al.*, 2008; Murugesan *et al.*, 2006; Mehta *et al.*, 2016; Bhalothia *et al.*, 2015]. Clay-plant waste based composites have been developed with the aim to facilitate clean drinking water to rural families at low cost. The ability of these porous clay composites for efficient removal of microbes and other chemically hazardous materials in distinct geographic locations have been widely studied [Yakub, 2012; Van *et al.*, 2009; Simonis and Basson, 2011; Plappally *et al.*, 2011]. The implication of industrial waste additive such as marble slurry on the arsenic removal efficiency and in improving the mechanical sustainability of such clay composites for water filtration is yet to be profitably explored.

Here, the marble slurry (industrial waste) added modified clay ceramics (MCC) were used as a mixed adsorbent unit. The raw materials (clay, sawdust and marble slurry) are easily available in almost all rural parts of Western Rajasthan, India. Based on the literature review, marble and clay have been individually investigated for their potential to remove toxic metalloids, however, the joint role of marble and clay in sintered ceramics as adsorbents has not been investigated, especially from modification of ceramic water filter composition design. Hence, an attempt is been made to evaluate the marble slurry added sintered ceramics as adsorbents for removal of arsenic from water media. The contact time of arsenic solution with the marble based ceramics (MCC) was examined to determine the saturation time for optimal arsenic removal. The pseudo second-order kinetic Eq. was applied in fitting the experimental batch test. Freundlich and Langmuir's model was used to study the adsorption at varying initial As (V) concentrations. The effect of varying pH of aqueous solution on the arsenic removal efficiency was determined. The mechanical sustenance of marble added clay ceramics was compared with clay ceramics without marble content using three-point bend test and compressive strength test.

6.2 MATERIALS AND METHODS

6.2.1 Raw Materials

The raw materials used to prepare ceramic adsorbent were clay, carpentry sawdust and marble slurry. The clay obtained from Raital, Mokalsar, near Jodhpur, Rajasthan, India, was placed on the cemented floor where it was crushed into very tiny particles using an iron hammer; the clay was then sieved to a very tiny particle size less than 0.5mm for investigation. The sieved clay was washed several times using distilled water and oven dried at 105ºC for 12 hours.

Large quantities of carpentry sawdust as a burnout material was availed from Rajasthan Timber Mart, Jodhpur, Rajasthan India. The sawdust was sieved to particles less than 1 mm (using 18 mesh sieve). The fine sieved sawdust was then stored in an airtight container to avoid pre-hydration before use.

Fine marble slurry as an additive was taken free of charge from marble processing industry located near Bherju Ji ka Than, Jodhpur, Rajasthan, India. The slurry was washed multiple times to remove unwanted dust or solid particles. The slurry was oven dried for 2 h at 125º C then cooled at room temperature, packed in stopper bottle and stored in desiccators for future use.

6.2.2 Preparation of adsorbent

The clay (C) , sawdust (S) and marble slurry (M) powders were manually mixed in the volumetric ratio of 45C:45S: 10M for 30 minutes to get a uniform consistency. The water as a binding agent was added to the dried mixture to form a wet ceramic body. The wet paste was shaped into two forms, 1) in the form of disc pellets of diameter 15 mm for conducting batch adsorption experiments and other in the form square plates for testing mechanical strength. The green body was hydro-plastically pressed at 1.5 bar pressure into a square prism ($100 \times 100 \times 15$ mm³) structure (as shown in **Figure 6-1**) using 50-ton axial hydraulic bench press (Model HBPO10, KEN-985-5000K, UK).

After shaping of ceramic samples, they were kept in ambient conditions till their weights were stabilized (a period of about eight days). The dry samples were then fired in a laboratory-type electrical furnace (Texcare™ Muffle Furnace, 1200oC, 250x340x180 mm³) at the rate of 2.5 C/min until 600° C, and then 10 °C/min until 850 °C
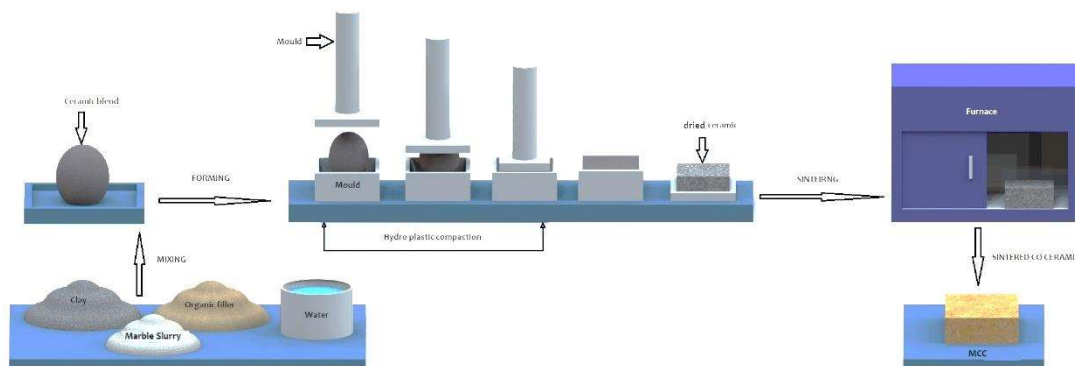

Figure 6-1 : Manufacturing of Clay Ceramics with marble as an additive

6.2.3 Preparation of Test Pre-filtrate

Standard stock solution of As (V) (100 mg/l) was prepared using $Na_2 HAsO_4. 7H_2O$ (A6756, Merck) in distilled water. The working standards were derived by serial dilution of stock in deionized water. The experiments were performed with aqueous solution of the following As (V) concentrations: 1 mg L^{-1}, 50 ug L^{-1}, 100 µg L^{-1}, 500 µg L^{-1} and 2000 µg L^{-1}. Atomic Absorption Spectroscopy was used for the analysis of arsenic (AA500 spectrophotometer, MRC Jaipur, India). 0.1 M solutions of HCl and NaOH were prepared in deionized water for pH adjustment.

6.2.4 Characterization of marble waste and ceramics

X-ray fluorescence (Bruker S4 PIONEER, JNU, India) was employed to evaluate chemical constituents of marble slurry and sintered ceramics. The crystal structure and mineralogy details were obtained by using Powder XRD (Bruker D8 Advance, IIT Jodhpur Facility) operated at 45 KV and 30mA using Cu Kα radiation (λ = 1.504 Å). Scanning electron microscopy (FEI Quanta) was used to assess the morphology of ceramics before and after filtration. Mercury porosimetry (Porosimeter AutoPore IV, IIT Bombay) was used to find the percentage porosity in the ceramic samples.

6.2.5 Batch Adsorption Studies

Batch adsorption mode was employed to conduct adsorption experiments at room temperature (25 ±1°C) in Teflon bottles.

6.2.6 Effect of contact time

Ceramic pellet of 5 gm was kept in test solutions. The pellet dipped solutions were shaken in a horizontal shaker (Wise Shake SHO -2D, Witeg) at an agitation speed of 80 rpm for all experiments. At the end of the desired contact time (5, 10, 15, 30, 45, 60, 90 min) bottles were removed from the shaker. The effect of contact time on the arsenic removal capacity of MCC ceramics was studied.

The equilibrium sorption capacity q_e was calculated using the Eq. (6.1) [Mlilo *et al.*, 2009]

$$q_e = (C_o - C_e)V/M \tag{6.1}$$

Here, C_o and C_e are the As (V) concentrations prior to and after As(V) adsorption (mg/L) respectively, V is the volume of the As(V) solution and M denotes the amount (gm) of the sorbent used in the reaction mixture. For determination of sorption rate constant the pseudo second-order reaction kinetics was used (Eq. (5.1), Eq. (5.2) and Eq. (5.3) [Ho and McKay, 1999].

6.2.7 Effect of initial As (V) concentration

Ceramics were tested by bringing them in contact with arsenic aqueous solution of distinct concentration (concentration of As(V) : 50 ug L^{-1}, 100 ug L^{-1}, 500 ug L^{-1} and 2000 ug L^{-1}) for 60 mins duration of time. The effect of distinct initial concentration was used to understand the mechanism of As (V) uptake. The atomic absorption spectral (AAS) data at varying As (V) concentrations were fitted to Freundlich (Eq. 5.4) and Langmuir isotherms (Eq. 5.5) to understand the adsorption behavior .

6.2.8 Effect of pH

The effect of pH in the range of 3–11 on the sorption capacity was investigated in a batch equilibrium adsorption experiment.

6.2.9 Microbial Removal

The 500 ml E.coli water solution was prepared using 5 ml bacteria and 495 ml distilled water. Filtration experiments were conducted in lab scale MCC and CC ceramic filters. 2 ml aqueous solution was collected in Eppendorf tube from influent and effluent water sample. The E.coli examination in the water sample was done as per the procedure documented in Standard methods for the Examination of Water and Wastewater [American Public Health Association (APHA)]

6.3 MECHANICAL TESTING

A 50-ton Universal Material Testing Machine (Model EZ-50, Lloyd Instrument, Germany) was utilized to perform compression and flexural strength tests [Plappally *et al.*, 2011; Mlilo *et al.*, 2009] of MCC and CC samples. The samples of span size 35 mm and 75 mm were tested at a loading rate of 1 Ns-1 for compression and flexural strength respectively.

6.4 RESULTS AND DISCUSSION

6.4.1 Properties of waste additive and ceramics

The chemical composition of the waste additive is given in **Table 6-1** in oxide form According to XRF analysis, the sintered ceramic contains a large fraction of silica as well as the oxides of aluminum, iron, calcium, magnesium and potassium. The waste marble powder contains major amount of calcium oxide followed by a considerable amount of silicon oxide. Loss on ignition of waste marble powder upon heating at 1000 °C was measured as 30.28%.

Table 6-1 : Chemical composition of the Marble additive and MCC ceramics

Constituents (%)	Marble Slurry	MCC
CaO	37.12	7.32
SiO2	10.566	65.435
Al2O3	1.574	16.682
Fe2O3	0.844	5.134
MgO	18.9	2.339
Na2O	0.192	0.964
K2O	0.524	2.126
LOI	30.28	-

The X-ray diffraction patterns for mineral phase contents of the waste marble powder and sintered ceramics are shown in **Figure 6-2**. The main phases in the waste marble powder are calcite (CaCO3), quartz (SiO2) and also minor dolomite (CaMg(CO$_3$)$_2$). The sintered ceramics includes quartz, potassium feldspar and calcite phases. The addition of marble has reduced the average porosity of the ceramics to 41.19 %, the average pore size was in the range between 1-5µm.
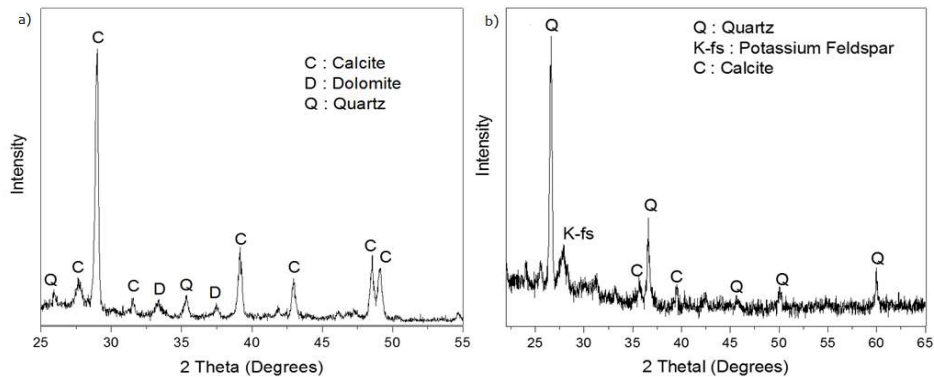
Figure 6-2 : XRD patterns of a) waste marble powder and b) sintered MCC ceramics.

6.4.2 Effect of time on adsorption

The results of time required to reach equilibrium for arsenic are shown in **Figure 6-3**. The arsenic contaminated water of 1 mg/L is in contact with 5 g MCC adsorbent for a distinct amount of time. The arsenic removal is plotted as a function of time in **Figure 6-3** at pH 8.0. **Figure 6-3** illustrated high As removal gradient in the first 30 minutes. Adsorption curve was observed to follow a birth process model with time (Plappally ey al. 2009). Removal rates were the largest at 60 min and then MCC got saturated. The short saturation time implies faster removal efficiencies
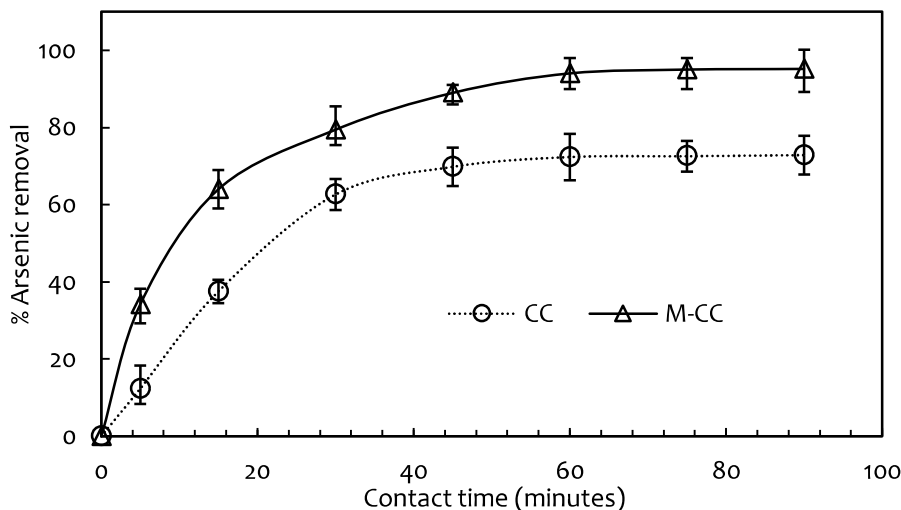
Figure 6-3 : Effect of contact time on arsenic removal efficiency of MCC ceramics

Initial concentration gradient between the dissolved arsenic and the number of vacant sites available on the MCC suggest rapid adsorption [Bhatnagar *et al.*, 2010]. The rate of removal starts to ebb due to a consequent decrease in reaction sites of the MCC surface with time.

Sorption studies on clay minerals, soils and other solid adsorbents used for arsenate removal have displayed similar faster kinetics in the initial stage [Zhang and Selim, 2005; Lee SM and Tiwari D, 2014]. The addition of marble slurry into the clay matrix has increased the calcite content, due to which, Ca^{2+} cations are likely to enhance As adsorption by forming positively charged surface. [Zehhaf *et al.*, 2015; Ghosh and Teoh, 1985]. The formation of Ca-As precipitates have been reported which promote As immobilization in soils [Meng *et al.*, 2000; Dutré and Vandecasteele,1995]

6.4.3 Pseudo Second order expression

The rate of As (V) adsorption on the ceramic in the 90 mins duration was investigated by plot between t/qt and time t (**Figure 6-4**). The second order constants for MCC were calculated using Eq. (5.1), Eq. (5.2) and Eq. (5.3) and were tabulated in **Table 6-2**. The adsorption capacity of clay ceramics with addition of marble slurry showed enhancement in comparison to clay ceramics without marble addition.
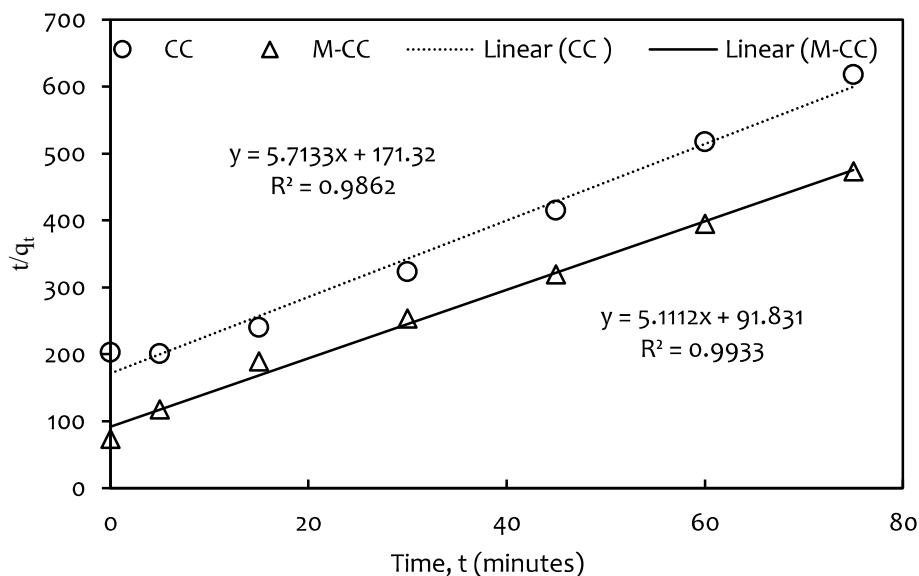
Figure 6-4 : Pseudo second order expression for MCC ceramics

The experimental kinetics data fitted well in the pseudo second-order kinetics model with a higher coefficient of determination (R^2 = 0.999). Also, the experimental value of q_e calculated experimentally came closure to theoretical q_e value 0.1956 obtained from pseudo-second-order kinetics model. This also indicates that the experimental data followed pseudo-second-order kinetics expression

Table 6-2 : 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.

Samples	q_e (mg/g)	K (g/mg min)	h (mg/g min)	R^2
CC	0.17503	0.190531152	0.00583703	0.9862
MCC	0.195618	0.356019509	0.013623607	0.9933

6.4.4   Surface Morphology

The microscopic study of the MCC porous ceramic prior to and after As treatment is shown in **Figure 6-5**. The micrographs revealed that MCC adsorbent had uneven surfaces with a large number of pores spaces. These surfaces would provide sites for adsorption of arsenic either physically or chemically.
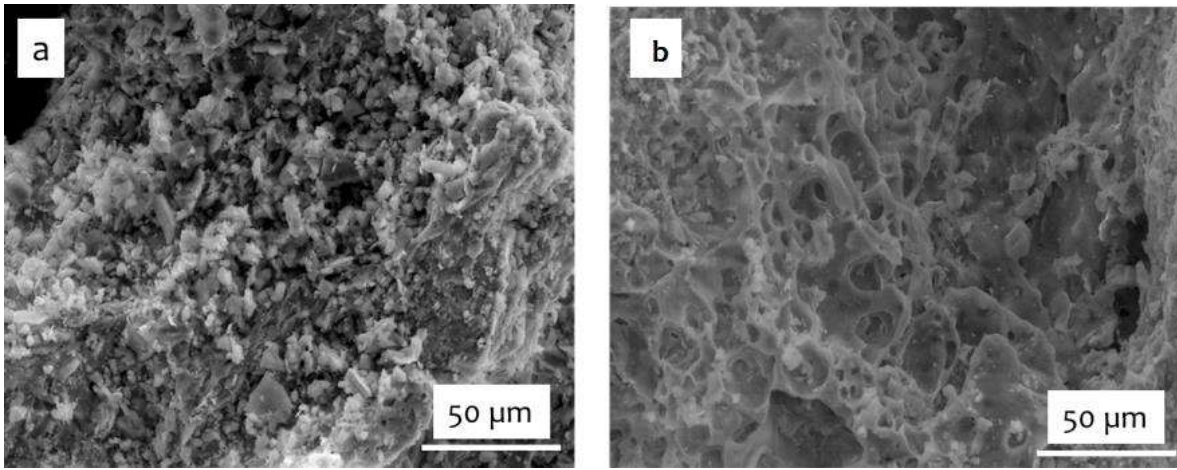
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Figure 6-5 : Surface morphology of MCC ceramics a) before and b) after contact time of 90 mins (20,000X)

Figure 6-5b illustrates the MCC surface after ninety minutes contact. The micrograph envisages pore closure with time due to adsorption and aggregation arsenic complexes on the rough and irregular ceramic surfaces.

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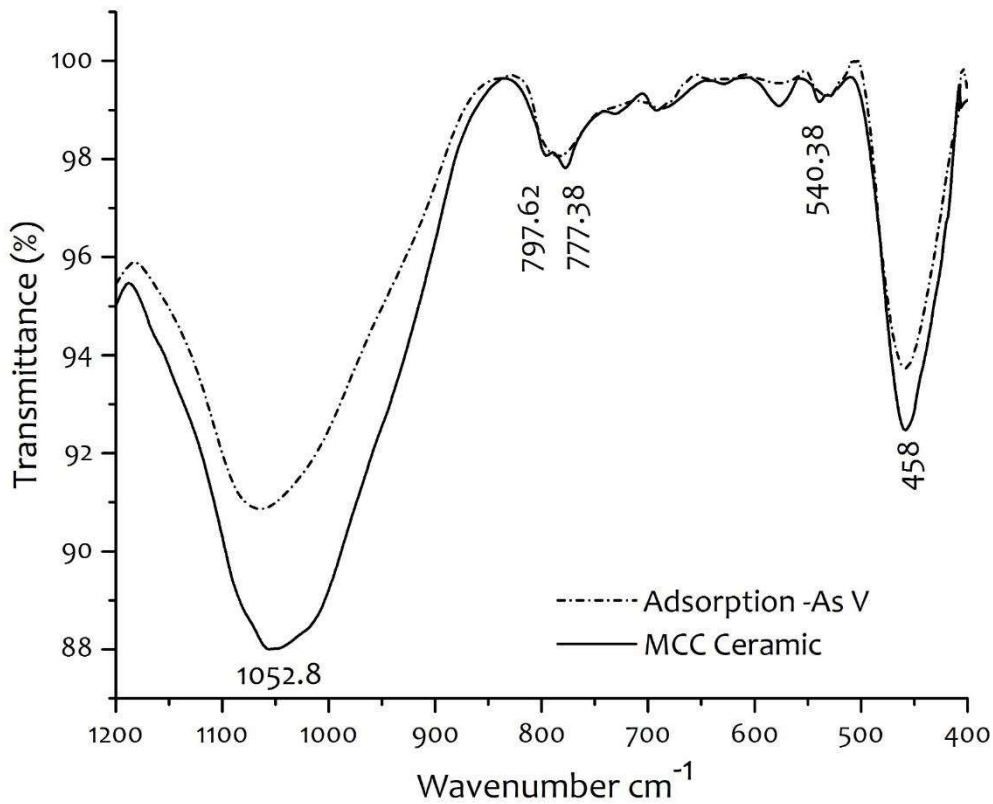

Figure 6-6 : FTIR spectrum of Marble slurry based ceramic (MCC) before and after As (V) adsorption

The FTIR spectra of the MCC adsorbent prior and post As (V) adsorption is displayed in **Figure 6-6**.The bands appeared at 1052 cm-1, 797.62 cm-1 and 777.38 cm-1 indicated stretching vibration of Si-O-Si group [Nayak and Singh, 2007; Petala *et al.*, 2013; Tandon *et al.*, 2013]. The

peaks at 540.38 cm^{-1} and 458 cm^{-1} resembled with Si-O-Al and Fe-O groups, respectively [Chen *et al.*, 2011; Li *et al.*, 2016]. The IR spectra of the MCC adsorbent after As (V) adsorption showed increased transmittance and reduction in stretching of corresponding peak bands. Such IR spectra could be a result of surface adsorption of As (V) on MCC adsorbent.

6.4.5 Effect of Initial Concentration

The effect of adsorbate concentration on arsenic removal was studied at different adsorbate concentrations of As (50 µgL^{-1}, 100 µgL^{-1}, 500 µgL^{-1} and 2000 µgL^{-1}) at an optimum pH of 8, 60 mins contact time and 1 gm adsorbent mass. The results (**Error! Reference source not found.**) indicated that arsenic removal efficiency decrease with the increase in concentration.
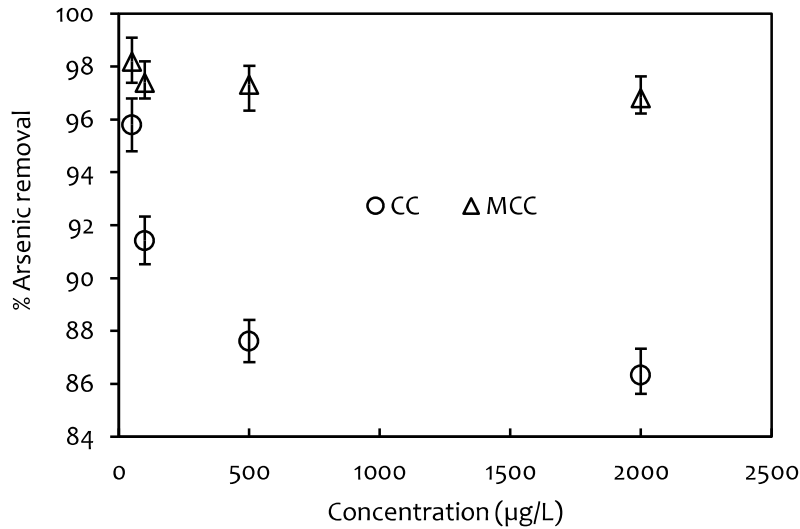

Figure 6-7: The influence of initial adsorbate concentration of As (V) removal using MCC ceramics

The transport mechanism of As to the MCC surface includes diffusion through the surface fluid film and diffusion through the pores in the media [Kamala *et al.*, 2005]. In the initial phase of adsorption, the As concentration gradient between the surface film and the pores was large. Therefore, the rate of adsorption accentuated. The rate of adsorption petered in the later stages due to the plummeting As diffusion into the MCC. At low concentration, the ratio of MCC area to the As concentration was large as a result of which As separation from aqueous volume was high [Kamala *et al.*, 2005; Say *et al.*, 2003].

The clay and marble additive in MCC jointly provided the more active surface of contact which promoted greater adsorption of metal ions at lower concentrations. The results indicated that adsorption efficiency of MCC was high at lower concentrations in comparison with CC ceramics. The behavior pattern is been consistent with the works done by other researchers [Fang *et al.*, 2005; Stipp *et al.*, 1992; Aziz and Smith, 1992; Aziz *et al.*, 2008]

6.4.6 Adsorption Isotherm

Equilibrium data, commonly known as adsorption isotherm are required for designing the adsorption systems. The equilibrium between adsorbed arsenic arsenic on the MCC ceramic was best described using the Freundlich adsorption model. The results of the model are discussed below.

Freundlich Isotherm

The equation of Freundlich empirical model is based on sorption on hetergeneous surface. The equation can be written as (Eq. (6.2)). The k_f and n are the Freundlich constant characteristics of the system [Ho and McKay, 1999].

$$ln\ q_e = ln\ k_f + (1/n)\ ln\ C_e \tag{6.2}$$

The linear plot between $ln\ q_e$ and $ln\ C_e$ showed that adsorption obeyed Freundlich model with a coefficient of determination of 0.995. The Freundlich constants, k_f and n, were enumerated from the intercept and slope of the plot (**Figure 6-8**). The parameter k_f indicates sorption capacity of the adsorbent and n describes the favorability of the adsorption process (**Table 6-3**) [Chassapis et al., 2010].
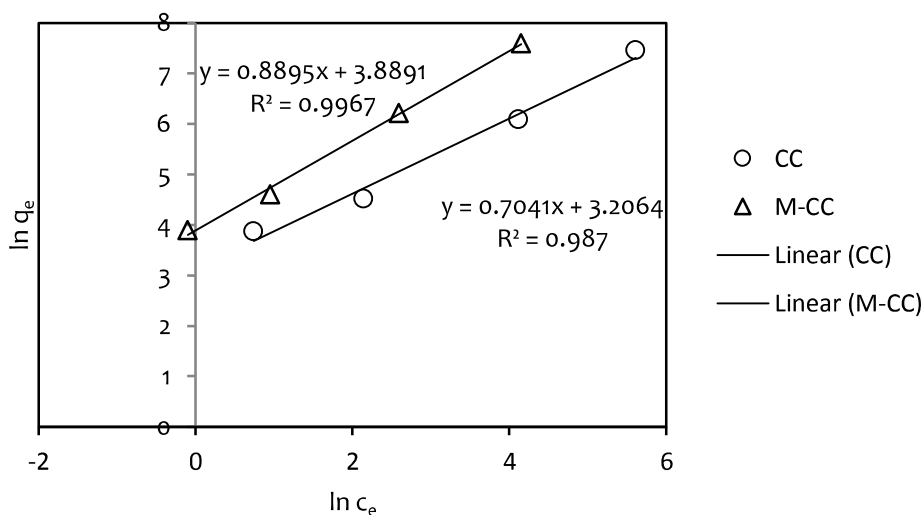

Figure 6-8: Freundlich Isotherm curve for MCC ceramics

The value of n lying between 1 to 10 represent beneficial adsorption. The adsorption capacity increased with the addition of marble slurry into the CC ceramics [Valko *et al.*, 2007; Chassapis *et al.*, 2010].

Table 6-3 : The parameters obtained from fitting the sorption data of As (V) onto various porous ceramics using Freundlich Eq. (6.2) and R is the regression coefficient for the linear plot.

Parameters	MCC	CC
n	1.12422	1.4202
$K_f\ [\mu g/g\ (L/\mu g)^{1/n}]$	48.86689	24.68504
R^2	0.9967	.987

6.4.7 Effect of pH

The effect of pH in the pH range between 3 to 11 on the removal of arsenic using adsorbent mass of 5 g for optimum 60 minute contact time was shown in **Figure 6-9**.

It was found As adsorption followed the parabolic profile. The arsenic removal using MCC material was low in acidic conditions. The efficacy of separation is found to increase with the increase in pH from 3 to pH 9. **Figure 6-9** illustrates the peak of arsenic contaminant removal

in an aqueous solution is at a basic pH of 9. The increase in the basic nature of the water decelerates As removal.
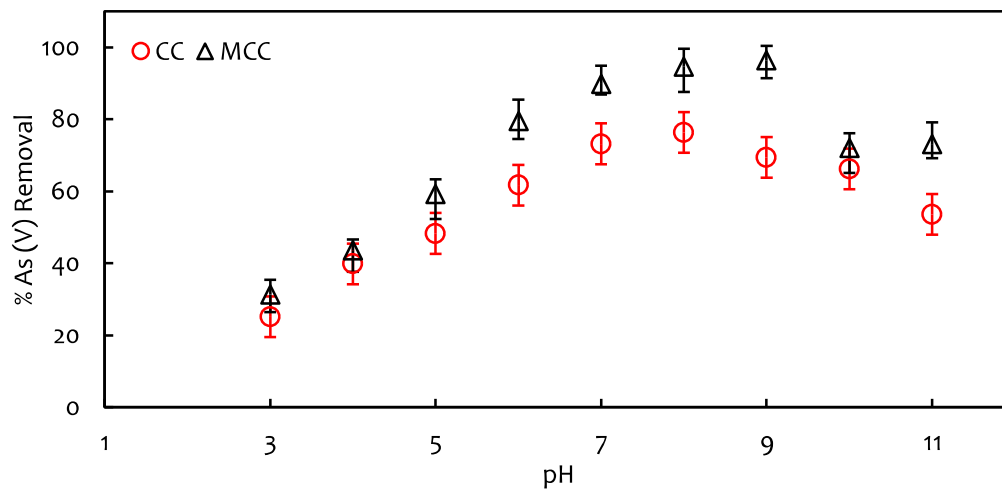

Figure 6-9: Effect of pH on arsenic removal efficiency using MCC ceramics

The improvement in adsorption of As (V) between acidic to neutral pH values may be due to the formation of As-Al and As-Fe complexes at the surface of MCC [Anderson *et al.*, 1976; Pierce, and Moore, 1982; Wilkie and Hering, 1996].The decrease in the adsorption behavior at extreme acidic and alkaline pH values was likely due to the hydrolysis of clay, which resulted in the dissolution of clay minerals [Goldberg, 2002]. Though the adsorption curve of the MCC and CC was found to follow same pattern, the As (V) ions showed higher arsenic (V) removal capacity between 3 to 9 pH values. For MCC the adsorption capacity slightly increased at beyond pH 10. This may be attributed to co-precipitation of As (V) due to dissolved calcium (due to marble slurry addition) as reported by other researchers [Hassan *et al.*, 2014; Escudero *et al.*, 2009; Bibi *et al.*, 2015].

The findings indicate that variation in pH influence the surface charge of the MCC, which positively influences the sorption kinetics and sorption capacity of the metal ions on the MCC surfaces [Fu and Wang, 2011].

6.4.8 Microbial Removal

The addition of marble into the clay ceramics has resulted in complete removal of E.coli from the effluent (**Table 6-4**). This is because of its antibacterial and antimicrobial properties [Ortega-Morales, 2018] which gives cent percent efficiency in removing E.coli from the filtered water sample.

Table 6-4 : E.coli removal efficiency of MCC

Sample	Initial concentration (I)	Final concentration (F)	I/F	Log Reduction Value (LRV) = $\log_{10}$ I/F	Final/ Initial	Efficiency of E.coli Filteration (1-F/I)
MCC	4×10^8	No viable E.coli trace found	-	-	0	1

6.5.8 Mechanical Characterization

The presence of high content of quartz and calcium carbonate in the marble added ceramics jointly attributed to the structural strength of the MCC (**Figure 6-10**).The calcium carbonate (from marble slurry) provided additional surface area for the nucleation and growth of hydration products which developed additional strength in MCC [O'Farrell *et al.*, 2001; Bentz, 2006]. The results resonated with the studies which involved incorporation of marble reject into ceramics for the construction and building materials application for better structural properties [Kavas and Olgun, 2008; Acchar *et al.*, 2006; Saboya *et al.*, 2007; Velasco *et al.*, 2014].
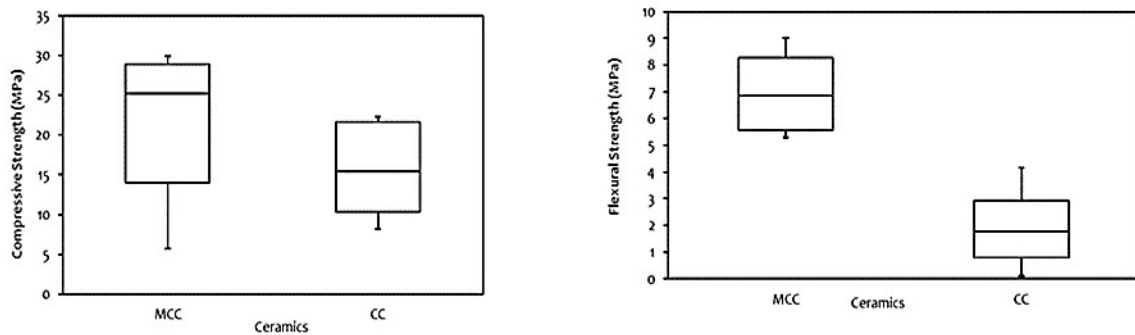

Figure 6-10 : Comparison of a) compressive (b) and flexural strength behavior of ceramics with (MCC) and without the addition of marble (CC).

6.5 CONCLUSION

The present study proposed marble and clay as low cost mixed adsorbents in sintered marble based clay ceramics. The main conclusions that can be drawn from the above study are given below:

1. MCC showed removal of 95.2% for arsenic from an aqueous solution of 1 mg/L of As with the contact period of 90 min.

2. The adsorption of arsenic on the surface of ceramics was approved (SEM image) from the smoothening of surface and covering of pores due to physical or chemical interaction at the surface.

3. The adsorption data fitted best to the Freundlich isotherm model, the value of $n > 1$ and k_f indicated increased adsorption capacity and rise in intensity of adsorption respectively.

4. The optimum pH was found to be 8 at which the highest removal of arsenic was obtained after contact period of 60 mins.

5. The structural integrity and mechanical sustenance of the ceramics greatly increased with the addition of marble slurry into the clay matrix.

6. The addition marble into the filter composition has enhanced the antimicrobial properties of the filters. Incorporation of marble encourages the use of ceramic filter units without silver coating. This would reduce the cost of the filter unit.