



## ARSENIC REMEDIATION OF DRINKING WATER

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### ABSTRACT

In this study, the potential of limestone as an adsorbent of different particle sizes for the removal of arsenic from drinking water was investigated. Effects of various operating parameters such as particle size, contact time and adsorbent dosage were studied using batch adsorption studies. X-ray fluorescence (XRF) was used to certify the mineral composition of limestone. This method shows maximum removal of arsenic 98.4 % under the following operating conditions: contact time 10 min, adsorbent dosage 2 g, and particle size 2  $\mu\text{m}$  and temperature 28 °C. Pseudo-first and pseudo-second-order kinetic models were employed to elucidate the adsorption behaviour of the system. The result of the adsorption process showed a poor correlation value with the pseudo-second-order model compared to the pseudo-first-order. This designates that the rate-determining steps in the adsorption of arsenic could be physical adsorption processes.

**Keywords:** Limestone, arsenic, adsorption, correlation, kinetics

### INTRODUCTION

The presence of hazardous anions in ground and surface water has led to serious pollution and has caused adverse health effects like cancer (Naushad *et al.*, 2017). These anions in drinking water are known to be toxic (Boparai *et al.*, 2011). Among these noxious anions, arsenic in water has been reported to be on the increase from different parts of the world including; as a result of this more than 55 million people are exposed to drinking water that contains high concentration of arsenic which exceeds World Health Organization's (WHO) limits (Erban, *et al.*, 2014). According to the report of Sorlini, *et al.*, (2014a), WHO recommended guideline value for arsenic in drinking water is 10  $\mu\text{g/L}$  which is not because it is safe to consume water containing less than that concentration of arsenic but because of the difficulty on its detection and removal (Kneebone *et al.*, 2000). The discharged of arsenic into the environment may be either via natural

activities and anthropogenic activities (Chakraborty, 2007). Arsenic occurs in both organic and inorganic forms; thus, the inorganic forms of arsenic is considered to be more toxic and are more prevalent in water compared to the organic form Sorlini, et al., (2014b; Sorlini, and Gialdini, 2014). Several remediation technologies like ion exchange, removal by filtration and precipitation/co-precipitation, coagulation/electrocoagulation, removal by adsorption onto artificial and natural sorbents, water softening with lime, membrane processes and bioremediation for arsenic removal in water have been developed (Reed, 2000, and Benhima *et al.*, 2008, Garrido-Hoyos *et al.*, 2013). But these treatment methods are available at industrial scale. However, alternatives for local treatment of water are scanty. These aforementioned technologies are found to be costly and required high energy consumption (Jain and Singh, 2012, Gencet *et al.*, 2003). Among the conventional methods, adsorption has been documented as the most promising, efficient and widely used fundamental method adopted in underdeveloped and developing countries (Altundogan and Tumen, 2003; Mondal, 2013). It is simple and economical for sequestering and recovering toxic metal ions from solutions. Therefore, the use of naturally occurring materials as low-cost adsorbents for removing toxic metals by researchers is still ongoing. The removal of arsenic contamination from mining wastewater using a readily available limestone as adsorbent was earlier studied by Webb and Davis (1999). Owing to this study, it is affirmed that the feasibility of using limestone for removal of arsenic from surface and groundwater is apparent (Sullivan *et al.*, 2010).

The investigation of adsorption capacities of limestone for the removal of arsenic has been made conventionally in this study. The present work explored the potential of limestone as an adsorbent in adsorption studies for removing arsenic from drinking water. The effect of various parameters such as contact time, the particle size of adsorbent and adsorbent dosage on the removal of arsenic was studied in order to disclose the performance evaluation of batch

adsorption studies. Furthermore, the emphasis was given to analyse the kinetic models.

## MATERIALS AND METHODS

Drinking water sample was taken from Boys, Girls and School premises of Ummaru Ali Shinkafi Polytechnic Sokoto State, Nigeria. The physicochemical parameters of the water were taken and arsenic level of the water was measured using atomic absorption spectrophotometer (AAS)

### Treatment of Limestone

Limestone was obtained from Kalambaina Village beside Sokoto Cement Factory, along Wamakko road Sokoto, Sokoto State. The limestone was rinsed several times using double distilled water to remove debris. The limestone was dried in an oven at 120°C for 24 hr. Thereafter, the dried sample was ground into a powder and sieved using different sizes of sieve.

### Effect of Contact Time

Batch adsorption experiment was conducted to determine the effect of contact time on the different sizes of the sieved (2 $\mu$ m, 4 $\mu$ m and 6 $\mu$ m) for the removal of arsenic in water. 1.5 g of limestone was shaken with 250 cm<sup>3</sup> of drinking water sample in 500 cm<sup>3</sup> conical flask using orbital shaker at 180 rpm at a contact time of 0, 10, 15, 20, 25 and 30 min. The solution was allowed to settle for 3 hours and then filtered using Whatman paper. The filtrate was analyzed for residual arsenic concentrations using atomic absorption spectrophotometer (AAS).

### Effect of Adsorbent Dosage

Batch adsorption experiment was conducted to determine the effect of varied dosage ranging from 2.0 to 4.0 g of limestone in 250 cm<sup>3</sup> of the drinking water sample. The various amount of adsorbent dosage (2, 2.5, 3, 3.5 and 4 g) was put into a conical flask and agitated using orbital shaker at 180 rpm for optimum contact time.

The solution was allowed to settle for 3 hours and then filtered using Whitman paper. The filtrate was analyzed for residual arsenic concentrations using atomic absorption spectrophotometer (AAS).

### Adsorption Analysis

The quantity of arsenic adsorbed and removal efficiency was calculated using equ. 1 and 2. The removal efficiency and adsorption capacity were obtained as follows:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100$$

(1)

$$q_e = \frac{(C_0 - C_e)V}{M}$$

(2)

Where  $C_0$  ( $\text{mg}/\text{dm}^3$ ) is the initial concentration of arsenic in aqueous solution,  $C_e$  ( $\text{mg}/\text{dm}^3$ ) is the concentration of arsenic aqueous solution at equilibrium,  $V$  ( $\text{dm}^3$ ) is the volume of the water used in the experiment, and  $M$  (g) is the weight of the adsorbent.

## RESULTS AND DISCUSSION

### Characterization

Table 1 shows the characteristic of groundwater sampling taken from UASPOLY Sokoto from the AAS analysis, it was found that the concentration of arsenic is  $1.052 \text{ mg}/\text{dm}^3$ . The value of Arsenic exceeded the acceptable limit of raw and drinking water standard.

### Brunauer-Emmett-Teller (BET) Analysis

$\text{N}_2$  adsorption-desorption analysis was used to determine the physical properties of surface area and porosity measurement of adsorbent (Limestone). The result of the BET surface area (BET) is shown in Table 1.

**Table 1: BET analysis of different particles size of limestone**

Sample	Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore diameter (nm)
LM 2µm	23.284	0.09421	8.113
LM 4µm	15.589	0.03942	4.968
LM 6µm	12.218	0.01931	3.752

### X-ray fluorescence analysis

X-ray fluorescence analysis was used to analyze the minerals and chemical composition of limestone as presented in Table 2. It was found that the limestone used in this study contained 98.93% of calcium trioxocarbonate (CaCO<sub>3</sub>) and 0.87 % of magnesium oxide (MgO). This shows that the limestone used in this study was approximately 99 % pure due to the combination reaction of calcium oxide and carbon dioxide. The high concentration of CaCO<sub>3</sub> and its solubility could help to enhance the removal of pollutant in drinking water sample through the precipitation process.

**Table 2: Mineral and chemical composition of limestone using XRF**

Mineral	Weight (%)
MgO	0.68
MnO	0.87
CO <sub>2</sub>	43.89
CaO	55.24

## ADSORPTION STUDIES

### Effect of Contact Time

The effect of contact time on the particle sizes of limestone on the removal efficiency of the arsenic in the drinking water sample was studied and presented in Fig. 1. Initial rapid adsorption was observed which reduced until the optimum time was attained. The presence abundant vacant sites on the surface of the adsorbent and the rapid occurrence are always controlled by the diffusion process from the bulk solution to the adsorbent surface, thereby attaining equilibrium. At these points, the rate of sorption is equal to the rate of desorption

and the equilibrium was achieved. It was observed that different optimum times were observed for the arsenic removal on the adsorbents. The equilibrium percentage adsorption of arsenic was 89.5 % (2  $\mu\text{m}$ ), 76.5 % (4  $\mu\text{m}$ ) and 75.3 % (6  $\mu\text{m}$ ) at contact time 10, 10 and 15 min. However, a further increase in contact time beyond the optimum time led to a decrease in the percentage removal of the arsenic which may be as a result of less available active sites for adsorption process.

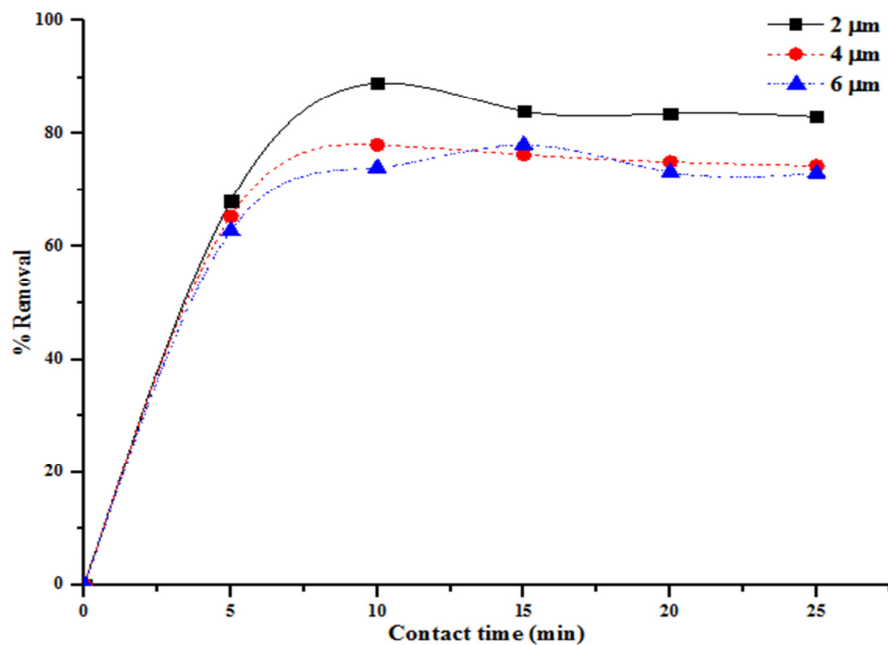


Figure 1: Effect of contact time on the adsorption of arsenic using different particle size of limestone.

### Effect of Adsorbent Dosage

The effect of adsorbent dosage on the removal of arsenic is shown in Fig. 2. Increase in the percentage adsorption of arsenic with an increase in adsorbent dose was obtained for the adsorbents. With an increase in dosage from 2.0 to 4.0 g an increase in adsorption of arsenic from 65.5 to 98.4, 57.3 to 95.4 and 56 to 90.2 % was obtained for 2  $\mu\text{m}$ , 4  $\mu\text{m}$  and 6  $\mu\text{m}$  mesh size of limestone, respectively. The increase is mainly due to an increase in the adsorptive surface area and the availability of more active binding sites on the surface of the

adsorbent. However, the maximum adsorption capacity of arsenic onto the adsorbents could be achieved from the batch experiment by the use of a laden amount of this adsorbent. It was concluded that by reducing the particle size of limestone, the removal efficiency increased. This might be due to the fact that by increasing the surface area of particles (Table 1) and the more the binding sites available, the more efficient will be the adsorption process.

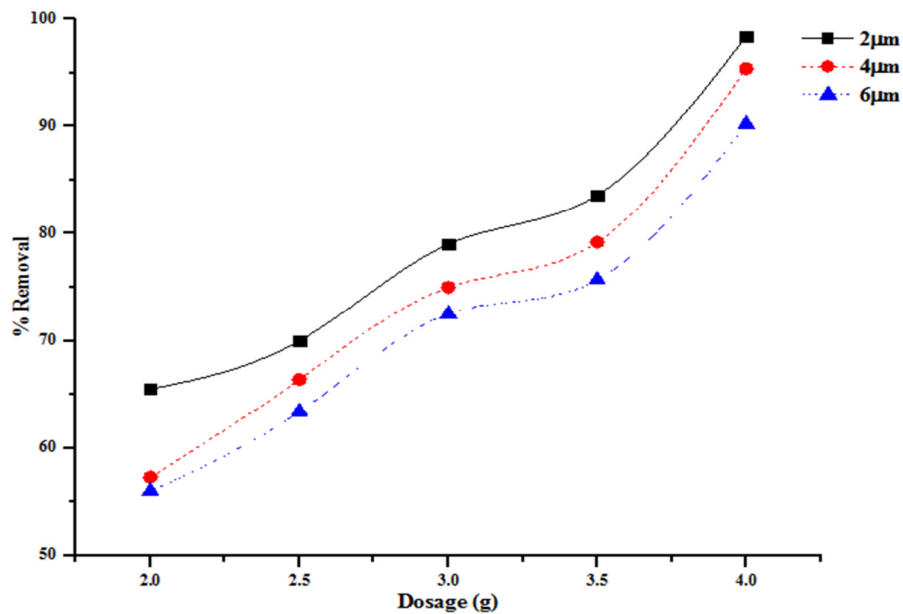


Figure 2: Effect of adsorbent dosage on the adsorption of arsenic using different particle size of limestone.

### Kinetics of the Adsorption Study

The kinetics models namely; first order and pseudo-second-order kinetic models were used to fit the experimental data and to also understand the rate law that best describes the removal of arsenic in drinking water using Limestone. The sorption kinetics defines the rate of the solute uptake at the adsorbent interface which provides an insight on the reaction pathways and mechanisms for the adsorption process. The kinetics of arsenic adsorption on the limestone was analyzed using pseudo-first and pseudo-second-order models.

### Pseudo-first-order model

The rate of the adsorptive interaction provides the adsorption process based on the unoccupied sites of the sorbent. The equation designated to this reaction is given as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where  $q_e$  and  $q_t$  are the amounts of metal ions adsorbed (mg/g) at equilibrium and at time  $t$  (min), respectively while  $k_1$  is the pseudo-first-order adsorption rate constant (L/min). The values of  $k_1$  and  $q_e$  were calculated from the equation and the correlation coefficient ( $R^2$ ) values of the equation model are presented in Table 3. The  $R^2$  values for the pseudo-first-order model is greater than 0.9 for 2  $\mu\text{m}$  particle size of limestone, suggesting that the adsorption processes of arsenic could be better explained by this adsorption mechanism.

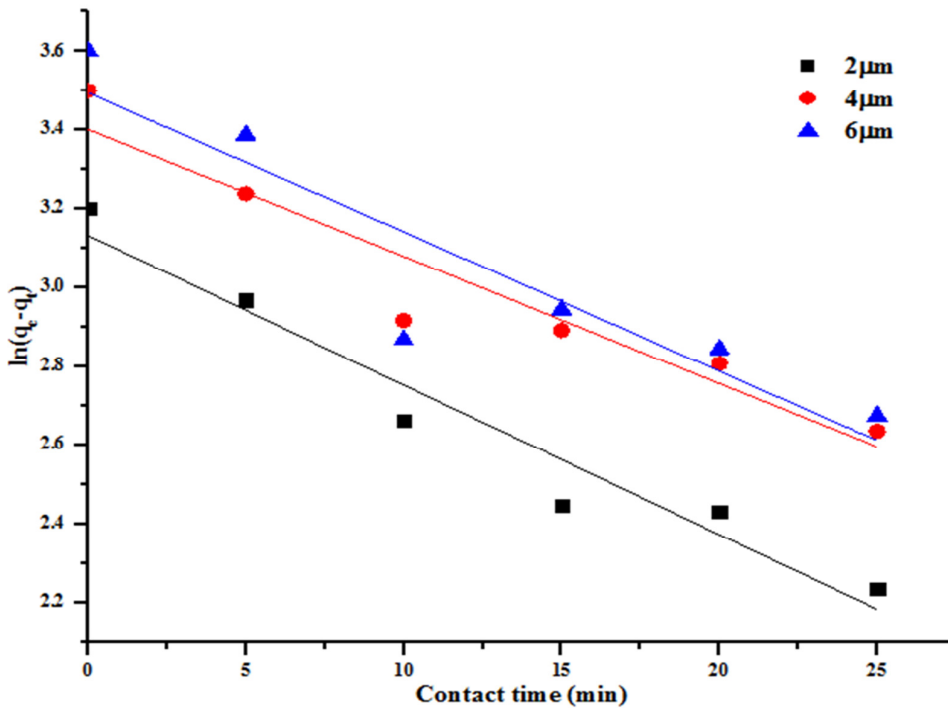


Figure 3: Plot of a pseudo-first-order kinetic model for the removal of arsenic from water



***Pseudo-second-order model***

Pseudo-second-order model predicts that the rate of adsorption rate is equivalent to the square of unoccupied adsorption sites. The model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Where  $k_2$  is the equilibrium rate constant for the pseudo-second-order (g/mgmin),  $q_e$  is the calculated adsorption equilibrium and  $R^2$  is the determined correlation coefficient as presented in Table 3. The values of the correlation coefficient from the linearized form of the pseudo-second-order model as presented in Fig. 4 were extremely low showing the poor quality of linearization. It is substantial from the result that the adsorption process showed poor compliance with the pseudo-second-order model compared to the pseudo-first-order. This indicates that the rate-determining steps in the adsorption of these ions in the study could be physical adsorption processes between the adsorbate and adsorbent.

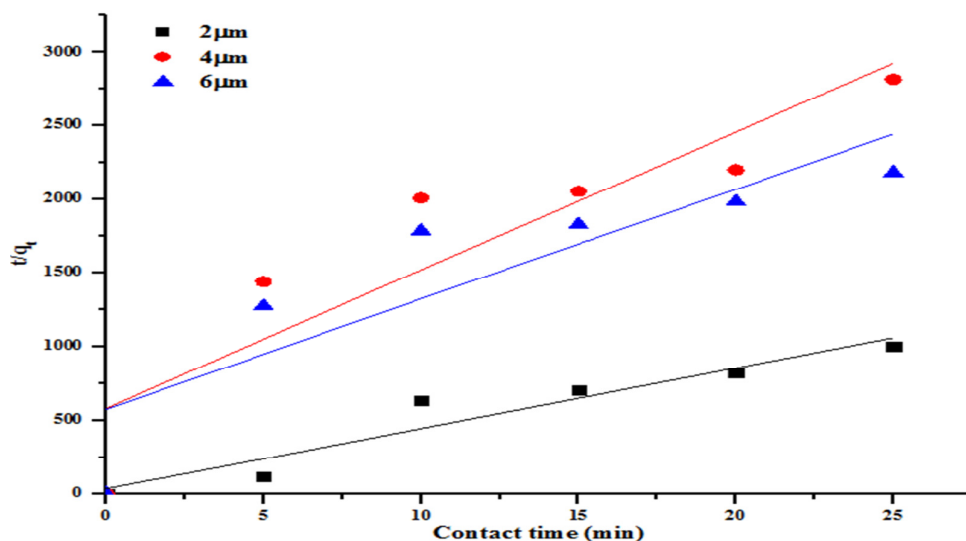


Figure 4: Plot of a pseudo-second-order kinetic model for the removal of arsenic from water.

**Table 3: Constants and correlation coefficients of pseudo-first-order and pseudo-second-order models of arsenic onto different particle size of limestone**

Model	Parameter	Particle size		
		2 $\mu\text{m}$	4 $\mu\text{m}$	6 $\mu\text{m}$
Pseudo-first	$k_1$ (min)	0.0380	0.0322	0.0353
	$q_e$ (mg/g)	0.412	0.682	0.772
	$R^2$	0.93774	0.89655	0.80963
Pseudo-second	$k_2$ (g/mg.min)	5.089	7.481	9.771
	$q_e$ (mg/g)	0.244	0.108	0.134
	$R^2$	0.90686	0.78311	0.70931

## CONCLUSION

The proposed batch adsorption study is an appropriate and suitable method for remove arsenic in water due to its simplicity and easy operation. The use of limestone in the present study as an adsorbent for arsenic removal is effective i.e almost 100 % arsenic removal. However, the adsorption was dependent on particle sizes, contact time and adsorbent dosage. The results of the kinetic study showed that pseudo-first kinetic better fitted the removal of arsenic. Therefore, it is believed that limestone as an adsorbent could serve as an alternative to the commercially available adsorbent for arsenic removal.

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