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Synthesis of Iron Oxide (Γ-Fe₂o₃) Coated Sand for Adsorptive Removal of Arsenic (iii) from Drinking Water

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Arsenic (As) contamination in the groundwater is mostly caused by Abstract: weathering of As-containing rocks, leaching of As-containing fertilizers, industrial effluents, etc. The most toxic form of arsenic (As) is arsenite (As(III)), which predominates in the reducing conditions in groundwater. Though the maximum permissible level of As for drinking water is 0.01 mg l-1 according to World Health Organization guidelines, 0.005 mg l⁻¹ is stated in the SLS of 614-2013. The ability of maghemite (y-Fe₂O₃) nanoparticles (NPs) to eliminate toxic metals from drinking water has generated a lot of interest. Direct use of iron oxide NPs may offer problems due to their propensity to aggregate in aqueous media. Therefore, y-Fe₂O₃ NPs are coated onto the sand used for water treatment. In this study, y-Fe₂O₃ coated sand was used as an adsorbent to remove As(III) from drinking water. The batch experiments were conducted at varying conditions of contact time, pH, and adsorbent dosage. Optimum removal efficiencies were found in 7 hours of contact time, neutral pH conditions, and 25.0 g l-1 weight of modified sand for fixed 1.0 mg l-1 of As(III) concentration. In the case of kinetic studies, the data reveals that the adsorption process follows the pseudo-first-order kinetics with an $R^2 = 0.980$ value. In adsorption isotherm studies, the data is fitted well with the Langmuir adsorption isotherm model $(R^2 = 0.99)$. The highest removal efficiency of As(III) was 99.1% was observed under above optimum conditions. In this study, the recovery of the absorbent of γ -Fe₂O₃ coated sand could easily be achieved by filtration process. The overall results ensure that the y-Fe₂O₃ coated sand acts as a low-cost adsorbent for the removal of As(III) from drinking water.

Keywords: γ-Fe₂O₃ coated sand; Adsorption; Adsorbent; Arsenic; Removal efficiency

1. Introduction

Arsenic contents in drinking water are varied depending on the kind of source (surface water, groundwater, precipitation), also regional conditions (Smedley & Kinniburgh, 2013).

Due to its non-ionic nature at the pH of natural water, As(III) is 25 – 60 times more toxic than As(V) and rather difficult to remove from water (Kango & Kumar, 2016b). Groundwater (tube well water/ well water) can be

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contaminated by highly toxic As(III) under reducing conditions. As an example, Bangladesh and West Bengal are most adversely impacted by the global arsenic situation especially due to the use of tube well water (under reducing conditions) for drinking purposes (Nordstrom, n.d.).

in The contamination of arsenic drinking water is a global problem, and arsenic-rich portable water has been found in many countries of the world. According to the World Health Organization (WHO) U.S. and Environmental Protection Agency (EPA), the Maximum Permissible Level (MPL) of arsenic for drinking water is 0.01 mg/L ppb) (Smith (10)& Steinmaus, 2011). Some arsenic-rich countries consider MPL in drinking water as 0.05 mg/L (50 ppb).

The problem of arsenic has been found in many countries like India, Nepal, Bangladesh, Myanmar, Thailand, Argentina, Pakistan, Mexico, the USA, and China (Sinha et al., 2011). Reports ensure, that over 100 million people drink arsenic-contaminated water, and 21% of reported deaths are caused by arsenic poisoning, Bangladesh and the nearby Indian province of Bengal are the most affected regions in the world because of the higher consumption of tube well water (Siddiqui & Chaudhry, 2017).

Drinking water can be contaminated with arsenic by both human activities and natural activities. Arsenic pollution in groundwater supplies is mostly caused by natural phenomena like weathering of arsenic-bearing minerals. The chemical and physical conditions of aquifers are more favourable for the transport and mobilization of arsenic than surface water sources. Therefore, more toxic and high arsenic concentrations have occurred in groundwater (Smedley & Kinniburgh, 2013).

In the dry zone area of Sri Lanka, Chronic Kidney Disease of unknown origin (CKDu) is a widely spread disease faced by people. It is thought that fluoride may be to cause of the condition in Sri Lanka's north central dry zone region, where high fluoride well water is present in locations where CKDu is common. A recent theory claims that CKDu is caused by either arsenic or cadmium (Kurisu et al., 2016). Arsenic has been identified as a potential etiological component for the newly rising pandemic known (CKDu) (tubulointerstitial nephritis), among rice farmers in Sri Lanka's dry zone. Analysis tests have revealed that these CKDu patients' biological samples (hair, urine, and nails) contain a considerable level of arsenic (Jayasumana et al., 2015).

A wide range of methods is used to remove arsenic from drinking water including Ion Exchange, Coagulation, Adsorption, Precipitation/Co-Precipitation, and Microfiltration. However, due to its great efficiency and cost-effectiveness, the adsorption method is the best approach among Adsorption surface them. is а phenomenon in which the adsorbate collects on the adsorbent surface. In recent vears, iron oxide-based nanomaterials have gained a lot of interest for their ability to remove heavy metals from wastewater. Iron oxide-based adsorbents have been studied extensively for removing arsenic from aqueous solutions which National Water Supply and Drainage Board, SRI LANKA

have a higher affinity to iron oxides(Byambaa et al., 2021).

Direct implementation of iron oxide NPs may present issues due to their proclivity to agglomerate in an aqueous medium, which gradually diminishes their efficiency over time. As a result, NPs connected to filter materials are taken into account (Kumar et al., 2008). River sand is the cheapest and most readily available of these materials Because of its thermal resilience, nontoxic nature, high biocompatibility, colloidal stabilization, adsorbents, chemical inertness, and changeable pore size. The sand was used in preliminary investigations and studies of the adsorption properties (Kango & Kumar, 2016c). Therefore, y-Fe₂O₃ NPs are coated onto the sand.

2. Material and Method

First, the natural river sand sample was crushed using a mortar and pestle. Then, the sand sample was separated into two different sizes using a sieve shaker.

Size 1 - Particle size < 0.5 mm (0.5 mm size)

Size 2 - 0.5 mm < particle size < 1.0 mm (1.0 mm size)

After that, the separated sand was washed thoroughly with 1 mol dm⁻³ of HCl acid using a vertical shaker for 12 hours to dissolve impurities. Next, the sand was washed with deionized water until the pH increased to 5.0. Finally, the sand was dried at 100 °C for 12 hours.

After that, (100.00 ± 0.05) cm³ of 2 mol dm⁻³ FeCl₃ solution and (25.00 ± 0.05) cm³ of 10 mol dm⁻³ NaOH solution were prepared. Then, 40.00 cm³ of FeCl₃ solution and 1.00 cm³ of NaOH solution

were poured over 100 g of purified dry sand and agitated gently. Then the mixture was heated at 90 °C for 3 hours in an oven. After cooling, again mixture was heated at 250 °C for 2 hours. After cooling, the coated sand was washed with distilled water and dried at 100 °C for 6 hours. (1st coating procedure). After cooling, again 40.00 cm³ of FeCl₃ solution and 1.00 cm³ of NaOH solution were poured over dry sand and heated at 90°C for 20 hours. Finally, the coated sand was washed with distilled water and dried at 100 °C for 6 hours. (2nd coating procedure) (Gogoi et al., 2018)

As(III) solutions were made in different concentrations using an appropriate mass of NaAsO₂ mixed with distilled water. Batch studies were carried out to find the optimum conditions for arsenic removal with various parameters. The parameters such as adsorbent size, adsorbent dosage, contact time, and effect of pH were investigated at room temperature with constant mixing (80 rpm).

For batch studies, 1 mg dm⁻³ of initial As(III) was prepared at pH = $(7.00 \pm$ 0.01), 0.25 g of adsorbent dosage, and a 7 hours contact time. After the equilibrium states. the final concentration of arsenic samples was measured by using Atomic Fluorescence Spectroscopy (AFS). Finally, the percentage (%) of arsenic removal efficiency was calculated using the following equation;

% removal efficiency =
$$\frac{C_0 - C_e}{C_0} \times 100$$
 %....

where C_0 and C_e are the initial and equilibrium arsenic concentration respectively.

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3. **Results and Discussion**

3.1 Characterization

Synthesized γ -Fe₂O₃ coated sand samples were characterized using an FTIR spectrometer, and X-Ray Diffractometer (XRD) to determine surface functional groups and bonds. For batch studies and column studies, Residual arsenic concentration was measured using AFS.



Figure 1 – FTIR spectrum for γ -Fe₂O₃ coated sand

Figure 1 shows that the FTIR Spectrum identified surface functional groups and binding sites of the γ -Fe₂O₃ coated sand. FTIR spectra of y-Fe₂O₃ coated sand peaks occur at 3100 cm⁻¹ due to O-H stretching vibration of the surfacebound water, 1770 cm⁻¹ due to C=O stretching (contaminated), 1465 cm⁻¹ due to C-H vibration (contaminated), 1245 cm⁻¹ Si-O-Si asymmetric stretching or bending vibration, 1077 cm⁻¹ for Si-O stretching vibration, (690 -790) cm⁻¹ due to Fe-O-O-H vibrations, and (450-460) cm-1 due to Fe-O stretching vibration.

Figure 2 shows the XRD pattern of the γ -Fe₂O₃ coated sand was shown in figure 2. Some peaks have been shown due to Si-O bonds due to the river sand. The Si-O bond represents a 2 θ value at 21°, and 50° positions with (111) and



Figure 2 – Illustration of XRD patterns for γ-Fe₂O₃ coated

(420) hkl values respectively. The characteristic peaks of γ -Fe₂O₃ are shown at 27°, 35°, 36°, 46°, 55°, 60°, and 76° 2 θ value positions with (211), (311), (222), (420), (422), (440), (533) hkl values respectively.

3.2 Synthesized γ -Fe₂O₃ Coated Sand



Figure 3 – γ -Fe₂O₃ coated sand (1.0 mm size)



Figure 4 – γ -Fe₂O₃ coated sand (0.5 mm size)

3.3 Batch Experiments

Table	1	-	Supplied	conditions	for
Optim	iza	tio	n of size ar	d dosage.	

Conditions	Controlled Parameters
Temperature	Room temperature
pН	7.0
Time	7.0 hours
As(III) concentration	1.0 ppm

Table 2 - Supplied conditions forOptimization of pH.

Conditions	Controlled values
Temperature	Room temperature
Size and Dosage	$1.0~\text{mm}$ and 25 g $l^{\text{-}1}$
Time	7.0 hours
As (III) concentration	1.0 ppm

Table 3 - Supplied conditions forOptimization of time.

Conditions	Controlled Parameters
Temperature	Room temperature
Size and Dosage	1.0 mm and 25 g l ⁻¹
pН	7.0
As(III) concentration	1.0 ppm

Table 4 - Optimum conditions forAs(III) removal from drinking water

Conditions	Optimum values
Temperature	Room temperature
Size and Dosage	$1.0~\text{mm}$ and $25~\text{g}~\text{l}^{\text{-1}}$
pН	7.0
Time	7.0 hours

3.4 Kinetics studies

The kinetic studies were investigated in different time intervals under neutral pH, and 0.5 mg/L initial arsenic concentration. Kinetic studies provide the rate of adsorption and rate-determining step. The analysis data is fitted in pseudo-first order.

The equation of the pseudo-first-order model is following,

$$\log(q_e - q_t) = \log q_e - \frac{Kt}{2,303} \dots (2)$$

Where, q_e and q_t are the amounts of arsenic adsorbed per unit mass of adsorbent at equilibrium time (mg/g)and considered time (mg/g)respectively, K is the pseudo-first-order rate constant (min^{-1}) , t is the time (min). The plot between log $(q_e - q_t)$ vs t gives the linear relationship, which obtains k as the slope of the graph(Kango & Kumar, 2016a).

Figure 5 shows that the experimental data for As(III) fitted well with the pseudo-first-order kinetic model with R² values of 0.984. It reveals that the adsorption process is physisorption (Van der Waals forces and diffusion)).



Figure 5 – pseudo-first order adsorption kinetics for As (III)

3.5 Isotherm studies

The adsorption isotherm describes the amount of arsenic adsorbed per unit weight of adsorbent with different equilibrium concentrations. That reveals the interaction between adsorbent and adsorbate in adsorption studies. Langmuir isotherm models are the common isotherm models that use adsorption parameters.

The equation of the Langmuir isotherm model is written as follows,

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \dots \dots (3)$$

Where, q_e is the amount of arsenic adsorbed per unit mass of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of arsenic in the solution (mg/l), K_L is the Langmuir constant, and q_m is the saturated monolayer adsorption capacity (mg/ g)(Kango & Kumar, 2016a).

Figure 6 shows the Langmuir isotherm graph for As(III). It is fitted with an R2 value of 0.975. Langmuir isotherm reveals the monolayer adsorption for As(III) on a homogeneous adsorbent surface.



Figure 6 – Langmuir adsorption isotherm for As (III)

4. Conclusion

The visual observation reveals that the 1.0 mm size y- Fe₂O₃ coated sand is more fully coated than the 0.5 mm size γ - Fe₂O₃ coated sand. Therefore, the 1.0 mm size adsorbent has a high removal efficiency than the 0.5 mm size adsorbent. The optimum adsorbent dosage is 25.0 g/l for the better removal of As(III). The pH is the main parameter for adsorption. The neutral pH level (normal drinking water pH) is the best pH for arsenic adsorption. The optimum time of As(III) is 7.0 hours.

Kinetic data have fitted to pseudo-first order model. Therefore, the adsorption of arsenic happens in physisorption. Isotherm studies reveal that the adsorption data are fitted for the Langmuir model. Therefore, monolayer adsorption happened while As(III) adsorption onto the adsorbent. The above findings ensure that the γ -Fe₂O₃ coated sand is an applicable adsorbent for removing both As (III).

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