



Removal of As(III) and As(V) from water by copper oxide incorporated mesoporous alumina

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ABSTRACT

In the present manuscript a new adsorbent namely copper oxide incorporated mesoporous alumina (COIMA) for removal of arsenic from water is reported. The COIMA was prepared by treating mesoporous alumina with copper sulphate solution followed by calcination at 450 °C in the presence of air. Various adsorption isotherm and kinetic parameters were computed using batch adsorption studies to determine the adsorption capacity for As(III) and As(V) and to understand the mechanism of adsorption. It was observed that incorporation of copper oxide improves the adsorption capacity of unmodified alumina from 0.92 to 2.16 mg g⁻¹ for As(III) and from 0.84 to 2.02 mg g⁻¹ for As(V). The results revealed that the adsorption follows Langmuir isotherm and pseudo-second-order kinetic models for both As(III) and As(V). The material is capable of simultaneously removing As(III) and As(V) with removal efficiencies of more than 95% for both As(III) and As(V). Assessment of the water quality before and after treatment with COIMA also confirmed that there is no leaching of copper and other parameters were also within permissible limits of Indian drinking water standard indicating that the COIMA can be used for treatment of arsenic contaminated drinking water.

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1. Introduction

Considering the ubiquitous nature of arsenic in the environment, human exposure to arsenic is inevitable. Exposure can occur via all three principal routes, that is, through inhalation of air, ingestion of food and water, and via dermal absorption. However, the most common and major source of arsenic exposure is contaminated ground water. Arsenic in drinking water predominantly exists as arsenite (As(III)) or arsenate (As(V)) of which As(III) is 25–60 times as toxic as As(V) and several hundred times as toxic as methylated arsenicals [1]. Worldwide, the degree of non-occupational exposure to arsenic varies greatly, being dependent on local geochemistry and the level and proximity of anthropogenic activity. The environmental health disaster due to excessive arsenic in drinking water is unfolding in many other countries including Argentina [2], Mexico [2], Australia [3], Bangladesh [4], Vietnam [5], Cambodia [5], etc. Countries where adverse health effects have been documented include Bangladesh, China, India (West Bengal), and the United States of America. In India alone millions of persons

in seven districts of West Bengal are drinking ground water with arsenic concentrations far above acceptable levels [6,7]. Thousands of people have already been diagnosed with poisoning symptoms, even though much of at-risk population has not yet been assessed for arsenic-related health problems.

The most important remedial action is prevention of further exposure by providing safe drinking water. In most of the areas source substitution may be impossible due to non-availability of alternate sources. Arsenic removal may be more appropriate in these situations. The cost and difficulty of reducing arsenic in drinking water increases as the targeted concentration lowers. It varies with the arsenic concentration in the source water, type of arsenic species, the chemical matrix of the water including interfering solutes, availability of alternative sources of low arsenic water, mitigation technologies, amount of water to be treated, etc. So far dearsenification has been attempted using several techniques including coagulation and filtration, ion exchange and membrane methods.

Extensive efforts are also being made worldwide to develop materials for selective adsorption of arsenic from numerous categories namely biological materials, mineral oxides, activated carbons, polymer resins, industrial byproducts/wastes, soils and sands, etc. [8]. In spite of extensive efforts, still there are many

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limitations of existing adsorbents that are restricting the success of adsorption based arsenic removal plants in actual field conditions, particularly the lower affinity for As(III) as compared to As(V).

It is therefore imperative to develop specially designed tailor made adsorbents for selective removal of arsenic from drinking water having equal affinity for As(III) and As(V), especially addressing the issue of safe disposal. Alumina in its various forms has also been studied extensively for removal of arsenic from water [9]. However, due to several limitations associated with alumina like low adsorption capacity, decrease in removal efficiency in the presence of interfering anions, narrow pH working range, etc. numerous modifications have been reported to overcome these limitations. Tripathy and Raichur [10] have reported enhancement in adsorption capacity of alumina by impregnation with alum. Incorporation of iron in its various forms on alumina is also reported to enhance the sorption properties of alumina [11,12]. Modification of alumina through incorporation of manganese oxide has also been reported to enhance the sorption of arsenic on alumina [13]. Very recently Martinson and Reddy [14] have reported adsorption of As(III) and As(V) by copper oxide nanoparticles showing that copper oxide is having high affinity for both As(III) and As(V). The authors have reported that the CuO nanoparticles effectively remove As(III) and As(V) in wide pH range and the presence of interfering ions namely silicate and phosphate does not interfere in the removal process [14]. Moreover, CuO has an advantage over other adsorbents since pH adjustments or oxidation of As(III) to As(V) is not required as a pre-treatment step prior to arsenic removal [14]. The effectiveness of CuO for arsenic removal was attributed to its high point of zero charge which is estimated to be 9.4 ± 0.4 [14]. The effectiveness of CuO for arsenic removal has also been evaluated using flow-through system and it was found that CuO effectively removed both As(III) and As(V) from groundwater without affecting the treated water quality [15].

The objective of the present study was to examine the efficiency of copper oxide incorporated mesoporous alumina (COIMA) for removal of As(III) and As(V) from water. Mesoporous activated alumina of high surface area was impregnated with copper oxide and used as an adsorbent in the adsorption process. The effect of incorporation of copper oxide on arsenic removal was compared with the unmodified alumina. Various parameters such as equilibrium isotherm, adsorption kinetics, adsorbent dose, effect of pH, interference of other ions and regeneration of adsorbent have also been investigated. Attempts were also made to study the effect of different anions commonly encountered in drinking water and to regenerate the saturated adsorbent to study its regeneration and reuse in multiple cycles.

2. Materials and methods

2.1. Materials

Granular AA (PURALOX) used for preparing COIMA was provided by SASOL, GmbH Germany. It was a high purity mesoporous alumina with pore size in the range of 50–200 Å. Spherical beads of alumina were used as such after washing with deionised (DI) water (18 MΩ resistivity, obtained from MilliQ DI water system). Copper sulphate, sodium chloride, sodium nitrate, sodium sulphate, sodium carbonate, sodium bicarbonate were purchased from E. Merck India Ltd. Stock solutions of 1000 mg l^{-1} As(III) and As(V) were prepared using arsenic trioxide and sodium arsenate and working solutions of different concentrations were prepared freshly by appropriate dilution of stock solution by DI water. All chemicals used in this study were of analytical grade.

2.2. Synthesis and characterisation of adsorbent

Unmodified AA was mixed with copper sulphate solution of different concentrations ranging from 0.001 M to 0.05 M. After addition of alumina, pH was maintained between 4.5 and 5.0 by adding 0.1 N NaOH and the mixture was kept on orbital shaker for 16 h. After shaking, the material was filtered and the solid residue was washed thoroughly with DI water to remove excess copper sulphate and kept for drying in air for 10 h. The dried material was calcined in air at 450°C for 4 h to convert the copper sulphate into copper oxide. The calcined material was again washed three times with DI water and air dried for 8–10 h. COIMA prepared using different concentrations of copper sulphate were evaluated and it was found that the COIMA prepared using 0.001 M gave the best arsenic removal efficiency and hence was selected for further studies.

COIMA was characterised thoroughly using PXRD, SEM, FTIR and surface area analysis. The PXRD patterns were obtained using benchtop X-ray diffractometer (Model Rigaku: Miniflex). The sample was powdered and scanned for 2θ ranges from 10° to 110° . The SEM analysis was done using Stereoscan S250 MK3 (Cambridge Instruments, UK). The surface area, pore size distribution and pore volume were obtained using Micrometrics ASAP 2010K surface area analyser using standard multipoint nitrogen adsorption isotherms.

2.3. Methods of analysis

Arsenic concentrations were determined by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Model: Perkin Elmer, Optima 4100 DV). Low concentrations (below $30 \mu\text{g l}^{-1}$) of arsenic were determined using graphite Furnace Atomic Absorption Spectrometer (GF-AAS, Model: Perkin Elmer) using palladium nitrate and magnesium nitrate as matrix modifier. pH was measured using pH meter (Model: Orion 909A). The concentrations of various co-ions and other physico-chemical parameters of treated and untreated water were determined using standard methods [16]. Carbonate and bicarbonate alkalinity and total hardness were determined titrimetrically. The analysis of copper was also done using ICP-OES. Blank experiments were conducted throughout the studies and majority of the experiments were repeated twice and it was observed that the experimental error was within $\pm 2\%$.

2.4. Batch adsorption and kinetic studies

The batch adsorption and kinetic experiments were conducted to study the optimum dose, equilibrium time, effective pH range, development of adsorption isotherms, kinetic modeling. Required quantity of COIMA was added to polyethylene bottles of 150 ml capacity with 50 ml of arsenic solution of desired concentration and pH. The bottles were kept on orbital shaker at 150 ± 10 rpm. The bottles were taken out at pre-determined intervals and contents were filtered using Whatman No-42 filter paper to separate sorbent and filtrate and the residual arsenic concentration were determined in the filtrate. The equilibrium time and optimum dose of the adsorbent were optimized by the method of continuous variation. Effect of contact time on adsorption was studied with initial arsenic concentrations of 1 mg l^{-1} . The effect of adsorbent dose was investigated by varying the dose of COIMA from 0.2 to 10 g l^{-1} for initial arsenic concentration of 1 mg l^{-1} . To study the effect of pH on arsenic uptake pH of the reactor after addition of sorbent was maintained using 0.1 N NaOH or 0.1 N HCl within a range of 2–12. All the experiments were conducted at room temperature $30 \pm 1^\circ\text{C}$. All experiments were duplicated with experimental error limit $\pm 5\%$ and average values are reported.

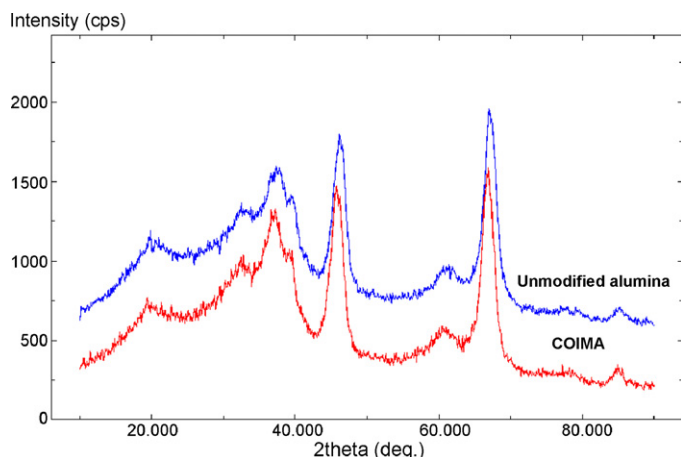


Fig. 1. X-ray diffraction pattern of unmodified alumina and COIMA.

3. Results and discussion

3.1. Characterisation of adsorbent

The PXRD patterns of unmodified AA and COIMA presented in Fig. 1 show broad peaks which are characteristic of amorphous phases of alumina. The presence of peaks at 2θ values of about 45° , 35° and 61° in both unmodified AA and COIMA confirms the presence of γ -alumina phases. Further, almost similar patterns of PXRD of unmodified AA and COIMA indicate that typical structure of alumina was retained after incorporation of copper oxide. The SEM images presented in Fig. 2a and b shows the surface morphology of unmodified AA and COIMA. The highly porous structure of alumina can be clearly seen in both unmodified AA and COIMA demonstrating that copper oxide has been evenly coated on the alumina surface without blocking the pores. Slight reduction in pore sizes was observed after copper oxide coating; however, the surface area measured using N_2 adsorption was same for unmodified AA and COIMA. The data pertaining to surface area, average pore size and pore volume of unmodified AA and COIMA are presented in Table 1. Copper oxide coating onto alumina resulted in minor reduction in surface area and average pore size which confirms that the copper oxide has been evenly coated on the surface of alumina without blocking the pores.

3.2. Adsorption studies

In order to study the dominant adsorption mechanism and to compute various adsorption parameters three isotherm models namely Langmuir, Freundlich and Dubinin–Radushkevich (D–R) were used. The Langmuir adsorption model can be represented in linear form as follows [17]:

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

The Freundlich model indicates the heterogeneity of the adsorbent surface and considers multilayer adsorption. The linear form of Freundlich adsorption model is as follows [18]:

$$\log(q_e) = \log k + \frac{1}{n} \log(C_e) \quad (2)$$

The D–R isotherm model considers more common features of adsorption and is not based on homogenous monolayer adsorption like Langmuir. The linear form of D–R isotherm model is as follows [19]:

$$\ln q_e = \ln Q_m - k_{ads} \varepsilon^2 \quad (3)$$

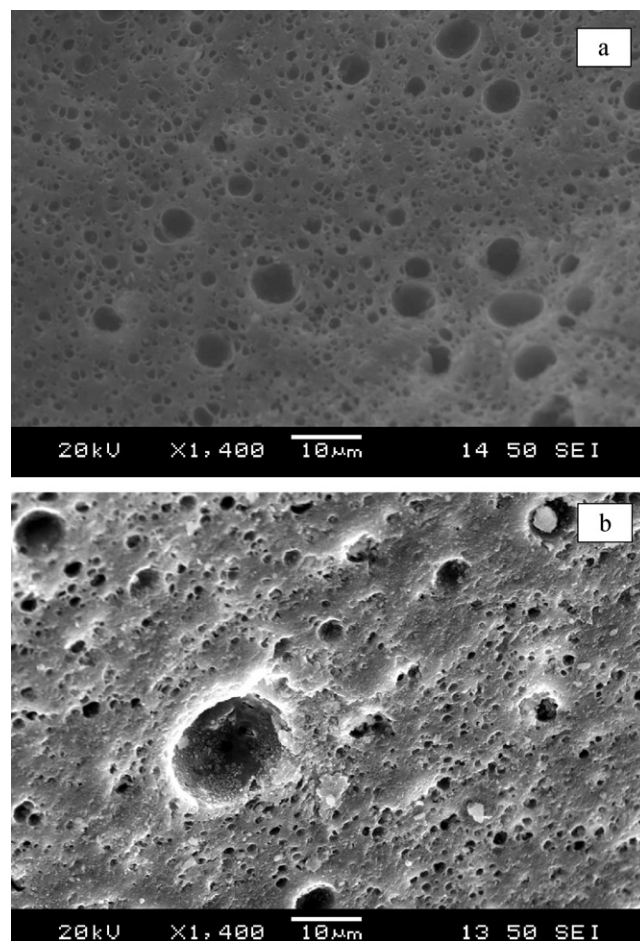


Fig. 2. Scanning electron micrograph (SEM) of (a) unmodified alumina and (b) COIMA.

and

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (4)$$

where q_e is the amount of adsorbate adsorbed per unit weight of adsorbent at equilibrium (mg g^{-1}), q_m is the maximum adsorption capacity (mg g^{-1}), K_L is the Langmuir constant, C_e is the equilibrium concentration of adsorbate in solution (mg l^{-1}), K_f is the Freundlich constant, n is the Freundlich constant, which reflects adsorption intensity, Q_m is the theoretical adsorption capacity (mg g^{-1}), k_{ads} is a constant related to adsorption energy, ε is polyanionic potential, R is gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$), T is temperature (K).

Results of experimental data were fitted to these three isotherm models to determine which model most accurately described adsorption by the adsorbent. The experimental data and Langmuir, Freundlich and D–R adsorption isotherm fits for As(III) and As(V) presented in Figs. 3 and 4, respectively. The results of various adsorption parameters obtained from these isotherm models are also presented in Table 2. On comparison of the fitness of the three isotherms it is evident that for both As(III) and As(V) the experimental data were well fitted to Langmuir model followed by Freundlich and D–R models signifying the monolayer adsorption of arsenic on uniform surface. The values of adsorption capacity for COIMA obtained from the Langmuir model was 2.161 and 2.017 for As(III) and As(V), respectively, which is significantly higher than that of unmodified AA (0.925 mg g^{-1} and 0.637 for As(III) and As(V), respectively, adsorption isotherms not shown). The significant increase in adsorption capacity after copper oxide coating is probably due to increased affinity of arsenic towards copper and

Table 1
Surface area, pore volume and pore size of unmodified alumina and COIMA.

Material	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (Å)
Unmodified alumina	189.12	0.4691	98.63
COIMA	189.25	0.4578	96.76

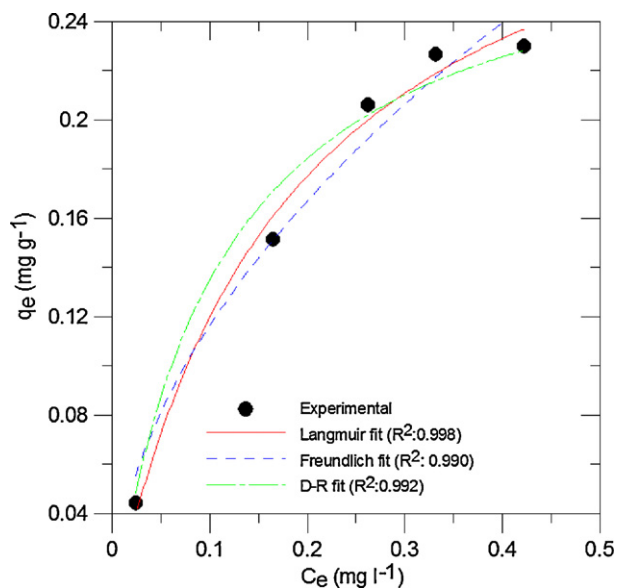


Fig. 3. Adsorption isotherms of As(III). (Batch volume: 50 ml, temperature: 30 ± 1 °C, initial concentration of As(III): 1.0 mg l⁻¹, contact time 24 h.)

also it is reported that metal oxide coating increase the zeta potential to more positive values resulting in enhanced anion sorption [13]. It is reported that the surface charge of alumina near neutral pH is between 15 and 20 mV whereas the surface charge of CuO at neutral pH is around 31 mV, which indicates that the incorporation of copper oxide on alumina alter the surface charge of alumina towards more positive values [14,15,20,21].

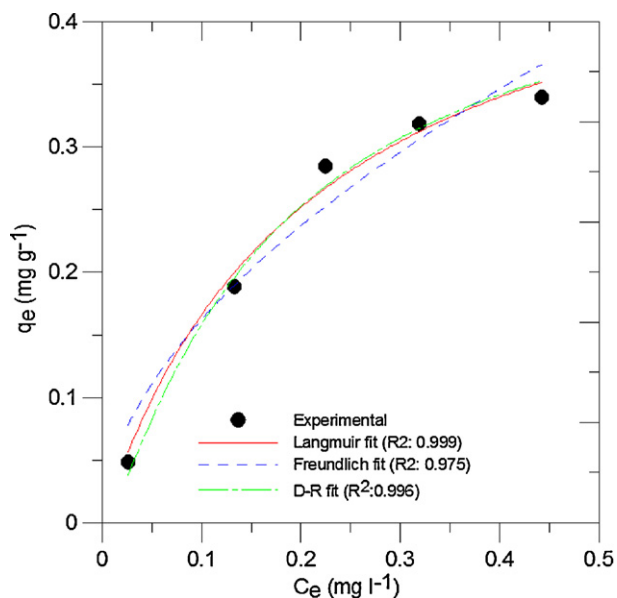


Fig. 4. Adsorption isotherms of As(V). (Batch volume: 50 ml, temperature: 30 ± 1 °C, initial concentration of As(V): 1.0 mg l⁻¹, contact time 24 h.)

Table 2
Adsorption isotherm parameters for arsenic adsorption onto unmodified alumina and COIMA.

Model parameters	Unmodified alumina	COIMA
Langmuir isotherm		
q_m (mg g ⁻¹)	2.161	2.017
K_L (mol l ⁻¹)	0.141	0.315
R^2	0.998	0.999
Freundlich isotherm		
K (mg g ⁻¹)	0.430	0.724
$1/n$	0.602	0.720
R^2	0.990	0.975
D-R isotherm		
Q_m (mg g ⁻¹)	3.620	2.3376
k_{ads} (mol kJ ⁻²)	2.23×10^{-8}	2.82×10^{-8}
R^2	0.981	0.963

3.3. Adsorption kinetics

Two main types of kinetic models frequently used to determine various kinetic parameters of the adsorption system are reaction based models and diffusion based models. To study the reaction kinetics pseudo-first-order and pseudo-second-order models were used. A simple pseudo-first-order kinetic model also known as Lagergren equation is represented as [22]:

$$\ln(q_e - q_t) = \ln q_e - k_{ad}t \quad (5)$$

where q_t is the amount of arsenic adsorbed at time t (mg g⁻¹) and k_{ad} is the equilibrium rate constant of pseudo-first-order adsorption (min⁻¹). The linearised plots of $\log(q_e - q_t)$ versus t will give the rate constants. The pseudo-second-order model is also commonly used to predict the kinetic parameters the linear equation for which can be written as [22]:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \quad (6)$$

and

$$h = kq_e^2 \quad (7)$$

where q_t is the amount of arsenic adsorbed at time t (mg g⁻¹), q_e is the amount of arsenic adsorbed at equilibrium (mg g⁻¹), h is the initial sorption rate (mg g⁻¹ min⁻¹). The values of q_e (1/slope), k (slope²/intercept) and h (1/intercept) can be calculated from the plots of t/q_t versus t .

The linear plots of pseudo-first-order (Eq. (5)) and pseudo-second-order (Eq. (6)) models for As(III) and As(V) are presented in Figs. 5 and 6, respectively. The values of k_{ad} , k and h and correlation coefficients obtained from the linear plots are also presented in Table 3. It is apparent from the values of correlation coefficients that fitness of the pseudo-second-order model is better as compared to pseudo-first-order model for both As(III) and As(V). It has been reported that the adsorption systems which follow pseudo-second-order model, chemisorption involving chemical bonding between adsorbent active sites and adsorbate valance forces is prevailing mechanism [22].

Sorption of a liquid adsorbate on porous solid adsorbent can also be modelled by pore diffusion models, which can be either particle diffusion or pore diffusion model. The particle diffusion model can

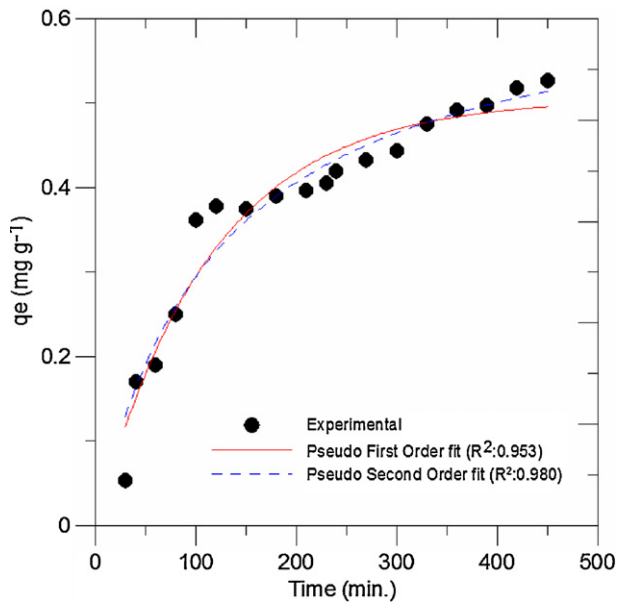


Fig. 5. Adsorption kinetic data of As(III). (Volume: 500 ml, temperature: $30 \pm 1^\circ\text{C}$, adsorbent dose: 0.4 g/l.)

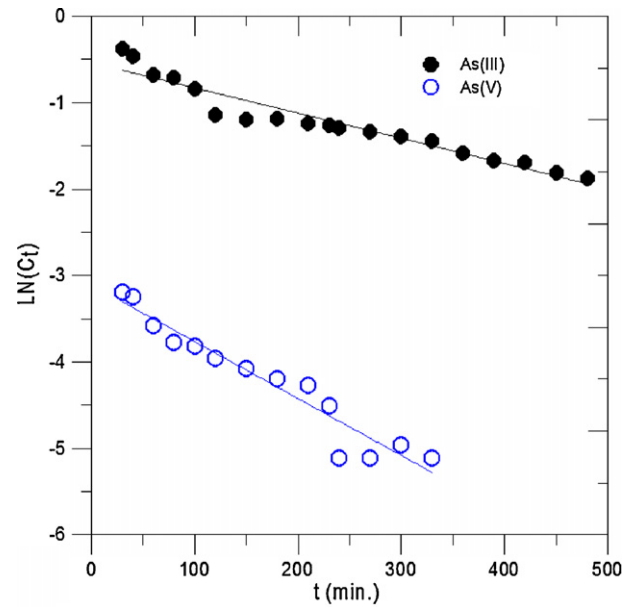


Fig. 7. Plots for particle diffusion model for arsenic adsorption by COIMA. (Volume: 500 ml, temperature: $30 \pm 1^\circ\text{C}$, adsorbent dose: 0.4 g/l.)

be written as [23]:

$$\ln\left(\frac{C_t}{C_e}\right) = -k_p t \quad (8)$$

where k_p is the particle diffusion coefficient (mg/g min). The value of k_p can be obtained by slope of the plot between $\ln(C_t/C_e)$ and t .

The intraparticle pore diffusion model given by Weber and Morris [23] is also commonly used to characterise the sorption data. According to this model, if the rate limiting step is diffusion of adsorbate within the pores of adsorbent particle (intraparticle diffusion) a graph between amount of adsorbate adsorbed and square root of time should give a straight line passing through the origin. The equation can be written as:

$$q_t = k_i t^{1/2} \quad (9)$$

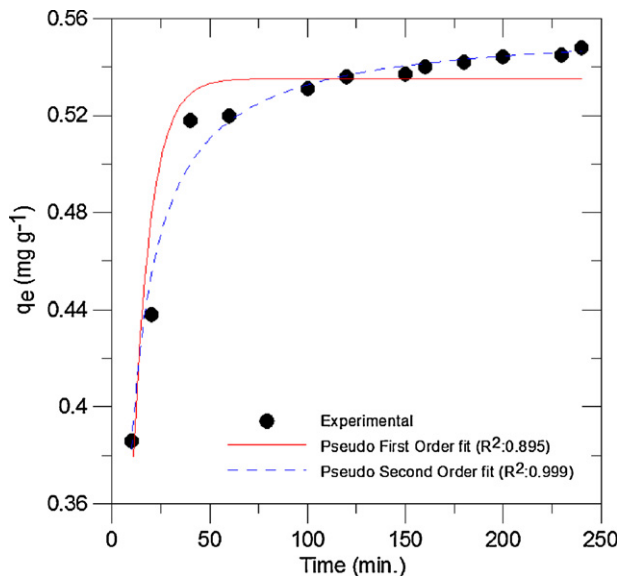


Fig. 6. Adsorption kinetic data of As(V). (Volume: 500 ml, temperature: $30 \pm 1^\circ\text{C}$, adsorbent dose: 0.4 g/l.)

where k_i is the intraparticle diffusion coefficient ($\text{mg/g min}^{0.5}$), which can be obtained from the slope of plot of q_t versus $t^{1/2}$. The plots of linear forms of particle diffusion and intraparticle pore diffusion models are given in Figs. 7 and 8, respectively for As(III) and As(V) and the values of different parameters are given in Table 3. The values of R^2 for particle diffusion model are closer to unity indicating that particle diffusion of adsorbate is contributing more towards rate determining step. However, in case of intraparticle diffusion model the lines are not passing through the origin, which reveals that the adsorption of arsenic on COIMA is a complex process involving surface adsorption, interparticle diffusion and intraparticle diffusion all contributing towards the rate of sorption.

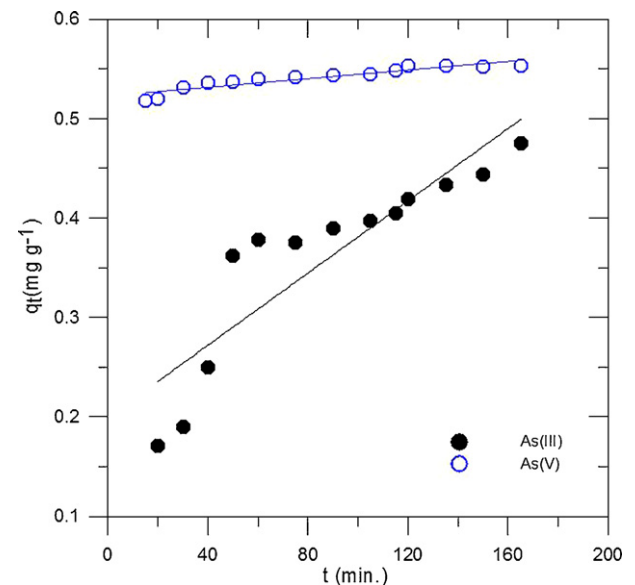


Fig. 8. Plot for intra-particle diffusion model (Weber–Morris plots) for arsenic adsorption by COIMA. (Volume: 500 ml, temperature: $30 \pm 1^\circ\text{C}$, adsorbent dose: 0.4 g/l.)

Table 3
Kinetic and diffusion parameters for arsenic adsorption onto COIMA.

Arsenic species	Pseudo-first-order		Pseudo-second-order			Particle diffusion		Intraparticle pore diffusion	
	K_{ad} (min^{-1})	r^2	k ($\text{g mg}^{-1} \text{min}^{-1}$)	h ($\text{mg g}^{-1} \text{min}^{-1}$)	r^2	k_p (min^{-1})	r^2	k_t ($\text{g mg}^{-1} \text{min}^{0.5}$)	r^2
As(III)	0.0021	0.954	0.011	0.0004	0.980	0.0031	0.933	0.002	0.807
As(V)	0.0054	0.895	0.4047	0.1251	0.999	0.0076	0.952	0.0004	0.834

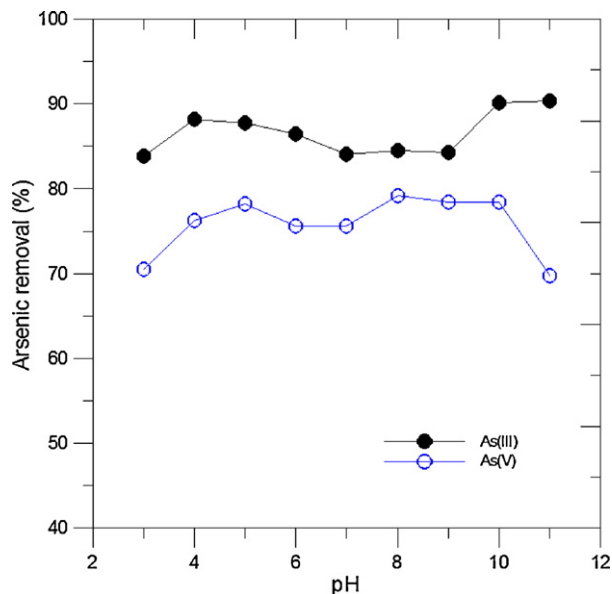


Fig. 9. Effect of pH on removal of As(III) and As(V). (Batch volume: 50 ml, temperature: 30 ± 1 °C, initial concentration of As(III) and As(V): 1.0 mg l^{-1} , contact time 24 h.)

3.4. Effect of pH

Removal of arsenic from water is highly dependent on pH and it has been observed that for most of the adsorbents adsorption capacity changes drastically with variation in pH. To study the effect of pH on arsenic adsorption capacity of COIMA, arsenic removal was studied at pH ranging between 4 and 9. As evident from Fig. 9 there is only slight variation in the arsenic removal with variation in pH which is in accordance with the results reported by Martinson and Reddy [14] for adsorption of arsenic on CuO. Marginal decrease in sorption capacities was observed at pH above 10 which may be due to competition by OH^- ions present in alkaline conditions. However, the final arsenic concentrations at all the pH values were below 0.05 mg l^{-1} which is below the permissible limits of Indian drinking water standards. Variation in pH as a function of time during the course of adsorption was also studied and presented in Fig. 10. It was observed that the pH varied from 6.5 to 7.2 during the course of adsorption till equilibrium is reached.

3.5. Effect of the presence of other co-anions

In order to study the effect of co-existing anions such as phosphate, sulphate, nitrate, carbonate and bicarbonate which compete in adsorption process, the adsorption studies were carried out in the presence of these anions. The initial concentration of arsenic was maintained at 0.5 mg l^{-1} and the concentrations of phosphate, sulphate, nitrate, carbonate and bicarbonate were 50, 100, 50, 100 and 100 mg l^{-1} , respectively. The effect of these anions on arsenic removal at different adsorbent doses is presented in Figs. 11 and 12 for As(III) and As(V), respectively. It was observed that removal of As(III) was marginally affected by the presence of these anions and the arsenic removal efficiency remained above 80%. However,

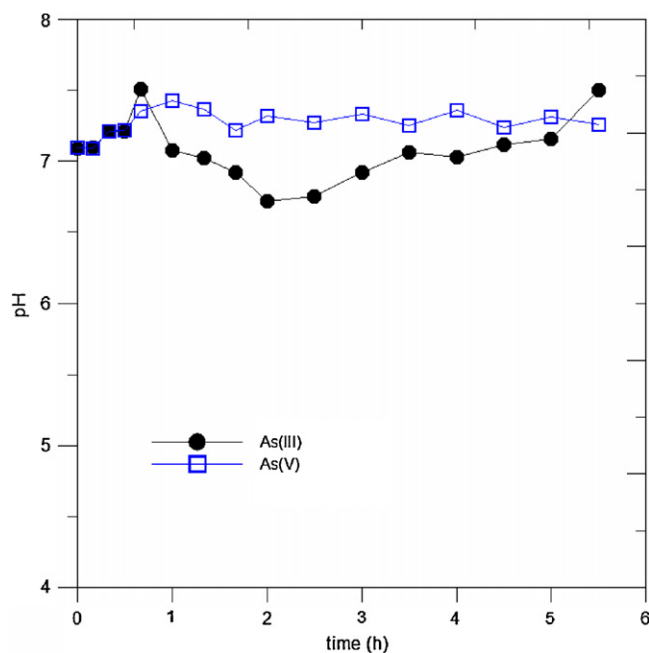


Fig. 10. Variation in pH during the course of adsorption of As(III) and As(V) by COIMA. (Volume: 500 ml, temperature: 30 ± 1 °C, adsorbent dose: 0.4 g/l .)

the presence of co-existing anions considerably reduces the As(V) uptake which may be probably due to the presence of phosphate which is reported to compete with As(V) [10]. Previous work on arsenic removal using CuO nanoparticles has revealed that CuO has

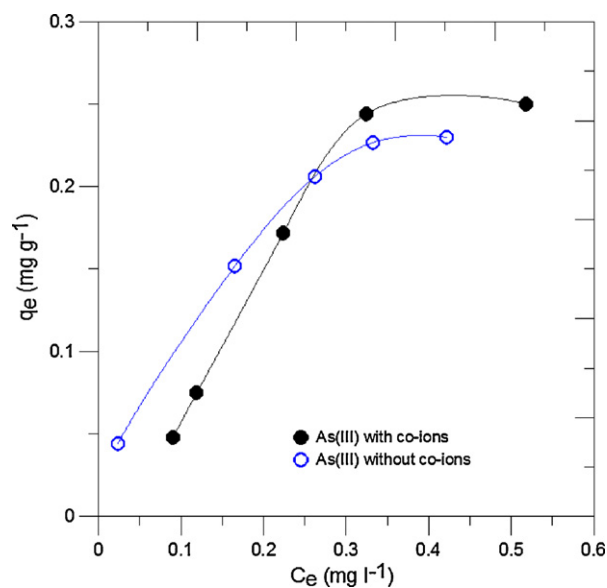


Fig. 11. Effect of different co-existing anions of removal of As(III) by COIMA. (Batch volume: 50 ml, temperature: 30 ± 1 °C, initial concentration of As(III): 1.0 mg l^{-1} , concentrations of co-existing anions (mg l^{-1}): PO_4^{3-} : 50, SO_4^{2-} : 100, NO_3^- : 50, CO_3^{2-} : 100, HCO_3^- : 100, contact time 24 h)

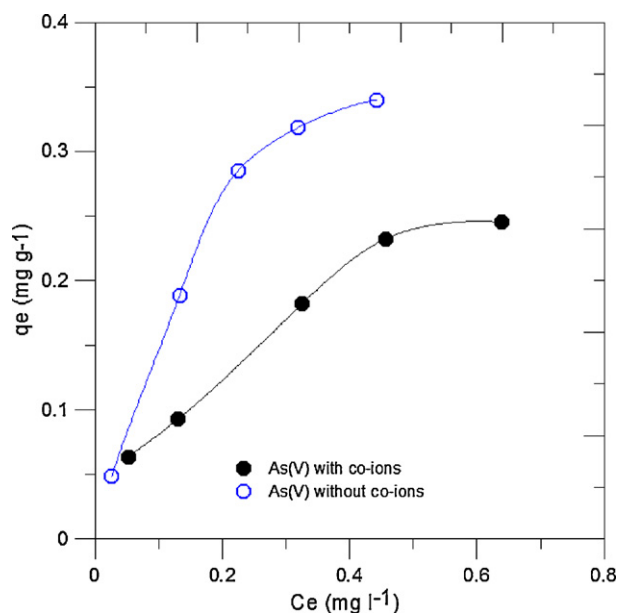


Fig. 12. Effect of different co-existing anions of removal of As(V) by COIMA. (Batch volume: 50 ml, temperature: $30 \pm 1^\circ\text{C}$, initial concentration of As(V): 1.0 mg l^{-1} , concentrations of co-existing anions (mg l^{-1}): PO_4^{3-} : 50, SO_4^{2-} : 100, NO_3^- : 50, CO_3^{2-} : 100, HCO_3^- : 100, contact time 24 h)

high selectivity for arsenic in the presence of anions namely phosphate, sulphate, silica, etc. [14]. The results of the present study also confirm the above findings and it was observed that COIMA has relatively higher affinity for arsenic as compared to anions namely sulphate, nitrate, carbonate and bicarbonate which are commonly encountered in groundwater.

3.6. Mechanism of arsenic removal

The FTIR spectra of unmodified alumina, COICA and As(III) saturated COICA are presented in Fig. 13. The FTIR spectra of unmodified alumina, COIMA and As(V) saturated COIMA shows sharp peaks at 1640 cm^{-1} and between 3300 and 3700 cm^{-1} which can be attributed to H–O–H bending and –OH stretching vibrations, respectively. The FTIR spectra of unmodified alumina and

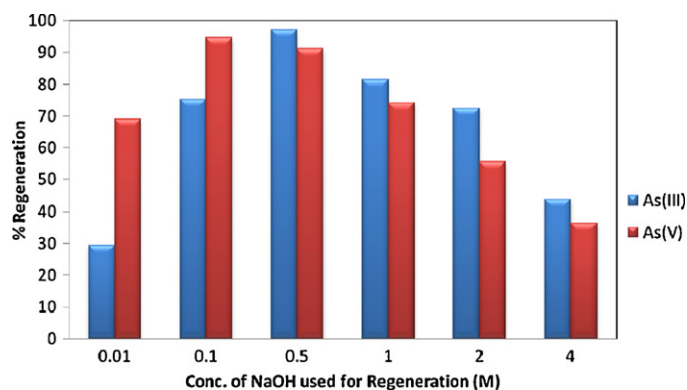


Fig. 14. Regeneration of arsenic saturated COIMA with various concentration of sodium hydroxide. (Initial arsenic concentration = 1 mg l^{-1} , adsorbent dose = 0.4 g l^{-1} , contact time = 1 h.)

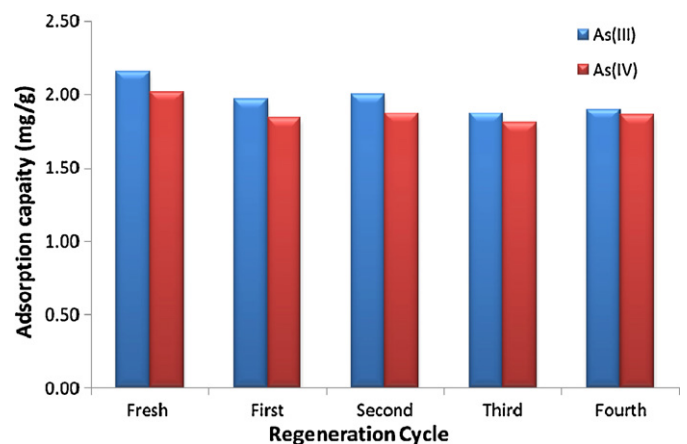


Fig. 15. Adsorption capacities after regeneration and reuse cycles. (Batch volume: 50 ml, temperature: $30 \pm 1^\circ\text{C}$, initial concentration of As(V): 1.0 mg l^{-1} , contact time 24 h.)

COIMA are almost similar except for a new band appeared at 1040 cm^{-1} which may be due to Cu–O vibrations. The spectra of As(V) saturated COIMA also exhibit bands at locations similar to unmodified alumina and COIMA. However two sharp bands located

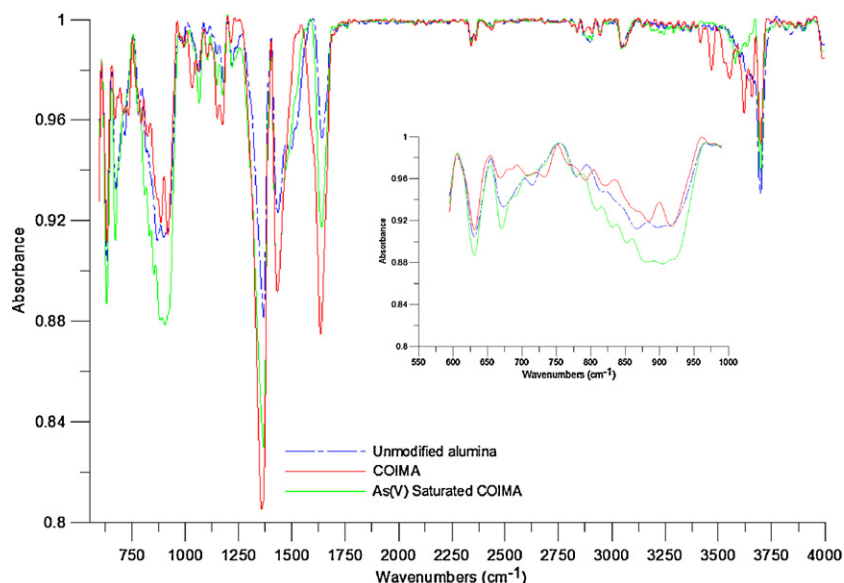


Fig. 13. FTIR spectra of unmodified alumina, COIMA and As(V) saturated COIMA.

Table 4Physicochemical parameters of water before and after treated with COIMA (volume of water: 500 ml, COIMA dose: 0.4 g l⁻¹, contact time: 24 h).

	Tap water spiked with As(III)	Tap water spiked with As(V)	Tap water spiked with As(III) after treatment with COIMA	Tap water spiked with As(V) after treatment with COIMA	Desirable limits as per Indian drinking water standard ^a
Turbidity (NTU)	2	3	4	4	10
pH	7.91	7.96	7.51	7.50	6.5–8.5
Alkalinity as CaCO ₃ (mg l ⁻¹)	76	76	48	55	600
Total dissolved solids (mg l ⁻¹)	161.4	161.4	148	150	2000
Total hardness as CaCO ₃ (mg l ⁻¹)	112	112	81	88	600
Calcium (mg l ⁻¹)	64	68	44	52	75
Magnesium (mg l ⁻¹)	48	44	37	36	100
Aluminium (mg l ⁻¹) ^b	BDL	BDL	0.024	0.041	0.2
Arsenic (mg l ⁻¹)	2.391	2.652	0.045	0.038	0.05
Copper (mg l ⁻¹) ^b	BDL	BDL	BDL	BDL	0.05

^a Indian Standard Specifications for Drinking Water (IS:10500).^b BDL: Below Detection Limit.

between 830 and 930 cm⁻¹ in spectra of unmodified alumina and COIMA merged into one broad band located at 880 cm⁻¹ which can be assigned to As–O symmetric and asymmetric stretching vibrations of the adsorbed arsenate species [24]. It is reported that bands positioned between 880 and 920 could be related to As–O vibration of an innersphere Al–O–As complexes and/or could be also due to As–O bonds of the adsorbed As(V) species on metal oxides [25]. Furthermore, significant decrease in intensity of peaks located at 1630 cm⁻¹ and between 3300 and 3700 cm⁻¹ which are characteristic of various H–O–H and –OH vibrations in spectra of As(V) saturated COIMA indicates that the arsenic sorbed on COIMA surface through replacement of the –OH groups. A similar spectrum was observed for As(III) saturated COIMA. It has also been reported that the adsorption of arsenic on amorphous metal oxides is through formation of inner-sphere surface complexes which are mainly attached as bidentate linkages with some monodentate linkages [26]. It has also been reported that adsorption following formation of inner sphere complex are not much influenced by pH and ionic strength [13]. Removal of arsenic by COIMA remains almost constant at different pH (Fig. 10) which also indicate that the adsorption of arsenic on COIMA is through formation of inner sphere complex through formation of As–O linkages.

3.7. Regeneration studies

Considering the practical applicability in field it is desirable that an adsorbent should be fully regenerated and reused so that it can be put into cyclic use in a cost effective manner. Regeneration of arsenic saturated adsorbents has been achieved using either alkali or strong acids including desorption of arsenic from metal nanoparticles. Reddy [27] has reported that arsenic saturated CuO nanoparticles can be successfully regenerated using sodium hydroxide. To study the regeneration, COIMA was first saturated with arsenic by shaking the adsorbent with initial arsenic concentration of 1 mg l⁻¹ and adsorbent dose of 2 g l⁻¹ for 24 h. Regeneration studies were conducted by shaking the required quantity of arsenic saturated COIMA with different concentrations of NaOH for 1 h. The results of regeneration studies is presented in Fig. 14. As evident from the results the amount of As(III) and As(V) leached increases with increase in NaOH concentration up to 0.5 M thereafter a decrease in arsenic desorption was observed. With NaOH concentration of 0.5 M almost all the As(III) and As(V) were desorbed (more than 95% regeneration) in 1 h resulting in complete regeneration of COIMA. The regeneration and reuse cycle were repeated for four times and results are presented in Fig. 15. As evident from the results that after four cycles of regeneration and reuse, the adsorption capacity of COIMA was remained almost constant for both As(III) and As(V). The adsorption capacity as obtained from fitting of Langmuir isotherms for As(III) and As(V) varied

between 1.87–2.0 mg g⁻¹ and 1.81–2.02 mg g⁻¹, respectively. The results of regeneration and reuse studies suggest that the COIMA can be used in a continuous flow through mode for removal of arsenic.

3.8. Treated water quality

In order to assess the potability of the treated water and to ascertain whether there is any leaching of copper into the treated water, normal tap water used for drinking purpose was spiked with 1 mg l⁻¹ of arsenic and was treated with COIMA. Various water quality parameters including copper were determined for treated and untreated water and are presented in Table 4. It was found that quality of the water after arsenic removal remained almost unaltered with slight change in pH and TDS. Also the copper was non detectable (detection limit below 0.9 µg l⁻¹) in the untreated and treated water confirming that there is no leaching of copper during the treatment. The values of various water quality parameters were compared with Indian standard for drinking water (IS:10500, 1992) and it was found that most of the values were below the permissible limits indicating that the COIMA can be used for treatment of arsenic contaminated drinking water.

4. Conclusions

The modification of alumina with copper oxide significantly improves the adsorption of arsenic. The adsorption isotherm data was best explained by Langmuir model and the adsorption capacity obtained from Langmuir isotherms was 2.161 mg g⁻¹ and 2.017 mg g⁻¹ for As(III) and As(V) which is significantly higher than unmodified alumina. The adsorption kinetics followed the pseudo-second-order model. The results of pH studies reveal that the COIMA can be used for removal of arsenic from water in broad pH range (between 4 and 10). The assessment of water quality after treatment confirms that there is no leaching of metals namely aluminium or copper. Moreover, other physico-chemical water quality parameters of treated water were within the prescribed limits indicating that COIMA can be used for removal of arsenic from drinking water.

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