A synergistic Cu-Al-Fe nano adsorbent for significant arsenic remediation and As(0) supported mitigation in aqueous systems

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ABSTRACT: In this work arsenic adsorption in aqueous systems is studied onto copper based ternary metal oxide (Cu-Al-Fe) nano adsorbents. In vibrational spectroscopy analysis, various As-O and As-OH related stretching vibrations were observed in 800–850 cm⁻¹ band. Adsorption kinetics study is observed with Pseudo Second Order (PSO) model and Freundlich model is observed for adsorption isotherms. Quantitative studies infer better As(III) adsorption in basic conditions and better As(V) adsorption in acidic conditions. XPS study of individual As(3d) spectra observed with multiplet peak behavior attributed various arsenic signals. In adsorbed systems significant proportions of As(0) signals are observed around 10 at.% for both As(III) and As(V) systems in pH 7 condition. Active redox behavior of Cu-Al-Fe resulted in better As(III) mitigation effect ability.

1 INTRODUCTION

Arsenic contamination in the South-Asian nations (India, Bangladesh, Pakistan etc.) is considered to be one of the largest mass poisoning incidents of human in history. This contamination scenario is affecting around 150–200 million population by means of different health disorders (Yan, 2012). Different types of arsenic remediation processes are in use for various purposes to reduce the final arsenic to less than 10 µg L⁻¹ (WHO guidelines). Adsorption based arsenic remediation method is considered to be one of the efficient and economical processes. Zero valent iron (ZVI) and pyrites (FeS₂) adsorbent systems were known for arsenic remediation by means of redox (i.e., simultaneous reduction and oxidation), surface complexation behavior and zero valent arsenic (i.e., As(0)) formation (Penke, 2016; Yan, 2012). The formation of As(0) onto adsorbent is useful in the prevention of post adsorption leaching effect of adsorbed arsenic back to the open environment. In this study we analyzed copper-based ternary metal oxides for arsenic mitigation by As(0) formation.

2 EXPERIMENTAL

CuCl₂·2H₂O (Loba Chemie, India), Al(NO₃)₃·9H₂O (Merck, India), Fe(NO₃)₃·9H₂O and Liq. Ammonia (A.R. grade, Qualigens Chemicals, India) of A.R. grade were used for synthesizing aluminum substituted copper ferrite as per the reported procedure. In preliminary qualitative studies, 100 mL aliquots of arsenic solutions (57.6 µg L⁻¹ for As(III) and 24 µg L⁻¹ for As(V)) were dispersed with 0.1 g of Cu-Al-Fe adsorbent and agitated for 24 h using an orbital

shaker at pH 7. The supernatant solutions were vacuum filtered using membrane filters. The separated adsorbent powders were dried and further preceded for IR, Raman and XPS studies. For XPS analysis of aliquot systems, filtered adsorption isotherms aliquots (C_i ~ 100 mg L⁻¹) were evaporated under natural conditions at R.T in open atmosphere and scratched samples were proceeded for characterization. The supernatant aqueous solutions were advanced to ICP-MS based quantitative analysis. In quantitative analysis adsorption isotherm (24 h), adsorption kinetics (6 h) and pH variation studies were performed. In all adsorption systems pH adjustment was done using standard HCl (1 M) and NaOH (1 M) solution.

3 RESULTS AND DISCUSSION

3.1 FESEM and vibrational spectroscopy results

After the arsenic adsorption agglomeration, and flocculation behavior was observed in adsorbent powders. This agglomeration and flocculation behavior which may be due to the formation of different immobilized arsenic species (As-O-M kind). This kind of studies were earlier reported for various metal-based (e.g., Fe, and Al) adsorbent systems. The weight percentage (i.e., EDS spectra) of arsenic onto these adsorbents is observed around 0.9 and 0.4 wt.% for As(III) and As(V) systems (Fig. 1). Vibrational spectra at pH 7 systems were observed with signals around 796, and 834 cm⁻¹ for arsenic (As(III), and As(V)) adsorbed systems (Fig. 1). These vibrational spectra signals observed in the 800–850 cm⁻¹ band inform the formation of various arsenic surface complex structures (e.g., As-O, As-OH) of ν and ν_{as} kind.

Figure 1. (a,b) FESEM, (c) IR and (d) Raman spectra of As(III), and As(V) adsorbed Cu-Al-Fe particles in pH 7.

Figure 2. As(3d) plots of Cu-Al-Fe in pH 2, and pH 12 ($C_i \sim 10 \text{ mg L}^{-1}$, $m: 0.4 \text{ g L}^{-1}$) (a,b) As(III)-pH 2, 12 (c,d) As(V)-pH 2, 12.

3.2 XPS results

The multiple peak behavior was observed in As(III) and As(V) adsorbed systems 43–45 eV in pH 7 confirms the occurrence of redox reactions.

In As(III) adsorbed systems, surface species corresponding to As(III) state were observed around 31.04 at.% whereas the remaining arsenic species were observed with less toxic As(V) state (~ 60.01 at.%). In As(V) adsorbed systems (pH 7) nearly 90 at.% of adsorbed arsenic was observed with As(V) state. Apart from these peaks an additional signals were observed in 39.5–40.5 eV band attributed to As(0) onto the adsorbent (Fig. 2). This behavior may be due to the reduction of adsorbed As(III) and As(V) species. In the total adsorbed arsenic around 9 at.% (As(III)), and 10 at.% (As(V)) of As(0) species were observed onto the adsorbent.

3.3 Mitigation results

The evaporated As(III) aliquot samples were observed with redox supported multiplet peak behavior corresponding to As(0) (50.5 at.%), and As(V) (49.5 at.%) (Fig. 3).

3.4 Adsorption mechanism

Our previous studies with Ni-Al-Fe and Co-Al-Fe were observed with a redox active behavior in arsenic remediation where cobalt systems were observed with As(0) (2–10 at.%) (Penke, 2016, 2017). The present study with copper-based Cu-Al-Fe adsorbent is observed with higher As(0) proportion (10–60 at.%) which is first of its kind for a copper-based metal oxide adsorbent (Fig. 4). The better arsenic remediation ability, significant As(0) formation (~ 60 at.%), and better

Figure 3. As 3d plots of evaporated As(III) aliquot samples in pH 7 ($C_i \sim 100 \text{ mg L}^{-1}$, $m: 0.4 \text{ g L}^{-1}$) (a) As(III) and (b) As(V).

Figure 4. Scheme of arsenic mitigation on to Cu-Al-Fe.

mitigation ability (90–100%) are due to the active redox potential behavior (E°) of Cu-Fe systems. In addition, aluminum (Al) substitution in Cu-Fe system also emphasized the arsenic adsorption behavior by enhancing the surface related properties.

4 CONCLUSIONS

Copper-based ternary metal oxides (Cu-Al-Fe) are verified for probable arsenic remediation systems from aqueous systems. The adsorption phenomena of As(III)/As(V) were evaluated using various spectroscopy tools. The outcome of the results suggest that better agglomeration behavior was observed in morphology study which is due to the formation immobile arsenic surface complexes. Redox active nature of Cu-Al-Fe synergistically enhanced the As(III) and As(V) mitigation through As(0) formation. A significant As(0) formation in XPS (at%) resembles the environmentally responsible adsorbent.

ACKNOWLEDGEMENTS

The authors would like to thank Indian Institute of Technology Kanpur (MHRD, Government of India).

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