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Screening of Metal Oxides and Hydroxides for Arsenic Removal from Water Using Molecular Dynamics Simulations

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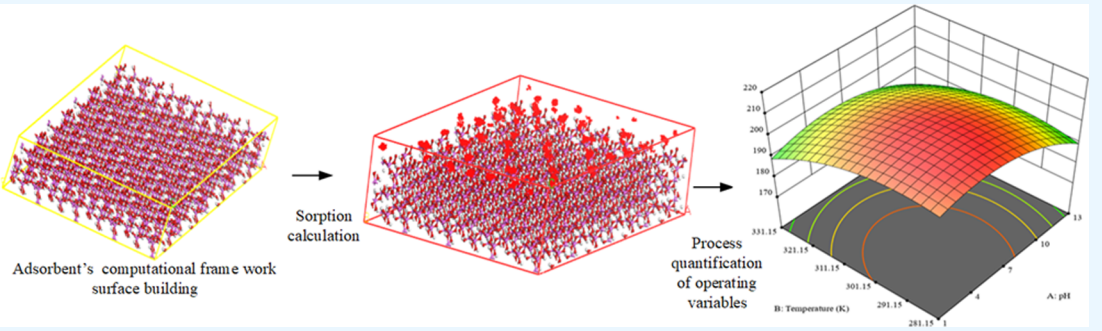

ABSTRACT: Arsenic in groundwater is a harmful and hazardous substance that must be removed to protect human health and safety. Adsorption, particularly using metal oxides, is a cost-effective way to treat contaminated water. These metal oxides must be selected systematically to identify the best material and optimal operating conditions for the removal of arsenic from water. Experimental research has been the primary emphasis of prior work, which is time-consuming and costly. The previous simulation studies have been limited to specific adsorbents such as iron oxides. It is necessary to study other metal oxides to determine which ones are the most effective at removing arsenic from water. In this work, a molecular simulation computational framework using molecular dynamics and Monte Carlo simulations was developed to investigate the adsorption of arsenic using various potential metal oxides. The molecular structures have been optimized and proceeded with sorption calculations to observe the adsorption capabilities of metal oxides. In this study, 15 selected metal oxides were screened at a pressure of 100 kPa and a temperature of 298 K for As(V) in the form of $HAsO_4$ at pH 7. Based on adsorption capacity calculations for selected metal oxides/hydroxides, aluminum hydroxide ($Al(OH)_3$), ferric hydroxide (FeOOH), lanthanum hydroxide $La(OH)_3$, and stannic oxide (SnO_2) were the most effective adsorbents with adsorption capacities of 197, 73.6, 151, and 42.7 mg/g, respectively, suggesting that metal hydroxides are more effective in treating arsenic-contaminated water than metal oxides. The computational results were comparable with previously published literature with a percentage error of 1%. Additionally, SnO_2, which is rather unconventional to be used in this application, demonstrates potential for arsenic removal and could be further explored. The effects of pH from 1 to 13, temperature from 281.15 to 331.15 K, and pressure from 100 to 350 kPa were studied. Results revealed that adsorption capacity decreased for the high-temperature applications while experiencing an increase in pressure-promoted adsorption. Furthermore, response surface methodology (RSM) has been employed to develop a regression model to describe the effect of operating variables on the adsorption capacity of screened adsorbents for arsenic removal. The RSM models utilizing CCD (central composite design) were developed for $Al(OH)_3$, $La(OH)_3$, and FeOOH, having R^2 values 0.92, 0.67, and 0.95, respectively, suggesting that the models developed were correct.

1. INTRODUCTION

Water contamination is a critical challenge at a global level. Drinking toxic water impacts millions of people worldwide, and our ecosystem has suffered consequently.[1] As population and industrialization rise, access to potable water becomes increasingly challenging.[2−4] Arsenic levels in many countries like Pakistan, Bangladesh, China, Taiwan, America, India, and Mexico are alarmingly high.[5−9] It has been classified as carcinogenic and poisonous.[10,11] It can cause liver, kidney,

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lung, and bladder cancer if ingested continuously, even in minute amounts (ppb).[12−14] The WHO (World Health Organization) current maximum allowable arsenic concentration in drinking water is 10 g/L (ppb).[15−17] Nonetheless, many developing nations continue to adhere to the previous guideline of 50 g/L due to inadequate infrastructure and costly water treatment technologies.[13] In July 2018, China hosted the seventh International Congress on Arsenic in the Environment, which included sustainable management and mitigation of arsenic removal.[18] The United Nations (UN) members stated an agreement on the 2030 Agenda for Sustainable Development, which aimed to guide national and international initiatives in the next 15 years, highlighting the importance of paying attention to arsenic removal so everyone has access to clean water.[18]

Several arsenic removal methods have been utilized, including coagulation, adsorption, ion exchange, and membrane separation.[15,19] Adsorption is thought to be the most appropriate and effective approach for removing toxins from water and wastewater due to its high effectiveness and low cost.[20,21] In this context, adsorption processes do not contribute to unwanted byproducts and have been found to be superior to other wastewater treatment methods in terms of ease of design and operation. Adsorbents of several kinds, such as zeolites, oxides, hydroxides, carbon-based materials, metal−organic frameworks, and clay, have been developed for the adsorption process.[20] Each adsorbent tends to remove pollutants from water and wastewater and has potential advantages. Adsorption is a surface phenomenon, and these adsorbents sorb the pollutants on their surface to remove them from water and wastewater.[22,23] The adsorption phenomenon arises from disparate or persistent attractive forces acting on the surface particles of the adsorbent material. Unlike the particles within the bulk adsorbent, these forces are not uniformly balanced. Consequently, the particles located at the surface of the adsorbent exhibit a notably elevated energy state compared to those situated within the core. Surface energy is this additional energy per unit surface area, and it is necessary for the attraction of adsorbate to its adsorbent surface.[24] The enthalpy and entropy are other important factors to be taken into account for adsorption.[25] Enthalpy and entropy are the measures of a potential sorption process.[25] The pollutants on adsorbents' surfaces are adsorbed, consequently being removed from contaminated water.[23]

Adsorption is one of the finest ways to remove arsenic from water with reported >95% quantitative efficiencies for arsenite and arsenate remediation. It is effective and affordable, does not require chemical addition, and is simple to use in developing countries with insufficient skilled labor and unstable electricity supplies.[26] These advantages of adsorption have encouraged many researchers to employ it to remove arsenic from drinking water.[12,27] In addition, adsorption is considered more adaptable than ion exchange, easier to run and safer to handle than the contaminated sludge produced by coagulation/precipitation, and cheaper than membrane separation.[28] Metal oxides/hydroxides, zeolites, and other adsorbents are commonly used in adsorption.[20] Among these adsorbents, metal oxides and hydroxides can eliminate arsenic more effectively, since surface functional groups, typical oxygen-containing groups, assist in its removal.[29] Arsenic removal involves chemisorption, forming inner-sphere complexes during the removal process in which As(V) directly binds to oxygen.[4]

Many experimental studies for arsenic removal from water have been reported by using different adsorbents. Initially, iron and $Al(OH)_3$ were investigated experimentally for arsenic removal from water.[30] Later, iron oxide ($F_{e2}O_3$) and aluminum oxide (Al_2O_3) were examined by experimental work, and it was found that they were effective by having maximum As(V) uptake values of 0.66 mg/g Fe_2O_3 and 0.17 mg/g Al_2O_3 at pH 6.[27] In a later study, the ultrafine Fe_2O_3 nanoparticles were experimentally checked for As(III) and As(V) adsorption, and it was found that Fe_2O_3 nanoparticles have adsorption capacities of 95 and 47 mg/g, respectively.[31] In another study, arsenic removal from water using FeOOH and Fe_3O_4 was studied, and it was observed that arsenic removal from water using iron oxides was pH dependent, and the maximum arsenic removal percentage was 80%.[32] Later, synthesized FeOOH was also studied for the adsorption of arsenic, in which the experimental equilibrium data were well represented by the Langmuir isotherm, and an estimated adsorption capacity of 76 mg/g was reported at ambient temperature, which was significantly higher than most of the adsorbents reported in the previous literature.[33] In a review, it was reported that for arsenic removal from water by adsorption using iron oxide, FeOOH was declared as a good adsorbent by having different adsorption capacities from 5 to 443 mg/g, which were highly dependent upon operating conditions, such as pH and temperature.[28] The removal of arsenic from water using iron-based adsorbents was reviewed, and it was concluded that iron oxides and hydroxides were effective adsorbents for arsenic removal.[34] In recent experimental studies, it was found that the arsenic adsorption rate is related to pH values. Arsenic adsorption was favored under acidic pH values and rapidly decreased in basic media.[35] In another recent work, Yoon et al. studied As(V) removal utilizing lignin and iron chloride to create biochar with low basicity and found highest As(V) adsorption, with a removal efficiency of >77.6% at the pH range of 3.0−10.[12] It was also mentioned that both the adsorbent and the adsorbate were involved in the adsorption process; this shows that As(V) was adsorbed by magnetite by a specific chemical reaction (chemisorption). As(V) binding to magnetite has been described as occurring mostly through chemisorption, which involves the development of bidentate inner-sphere complexes.[12] Xion et al. studied schwertmannites and akaganéites for the adsorption of arsenic ions from contaminated water and found that the adsorption of As(III) and As(V) was a rapid reaction, in line with the pseudo-second-order rate equation. It was also mentioned that iron oxyhydroxides exhibited exceptional adsorption capacities to arsenic species due to their abundant hydratable hydroxyl groups, which can form inner-sphere complexes with arsenic on their surface.[36]

Apart from performing experimental work for arsenic removal, many simulation studies have been done using molecular dynamics (MD) simulations.[37] The MD simulation allows for the microscopical study of the adsorption process within a sufficient time frame, budget, and space. Molecular modeling is currently regarded as a successful research method for elucidating the adsorption process.[20,38] MD simulations can produce effective techniques to simulate structures and elucidate the adsorption phenomenon at a molecular level by applying appropriate computational computations.[39,40] Moreover, recently, molecular simulations have evolved as a prominent technology for the screening of materials in industrial applications. It has been performed to circumvent

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