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Molecular screening of metal oxides for arsenic removal from water

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Abstract. Toxic metal arsenic in the ground water is poisonous and harmful that should be treated to ensure human health and safety. For many years, different technologies have been developed for the treatment of contaminated water and adsorption is an economical method in which a large number of adsorbents are being used including metal oxides. The selection of these metal oxides needs to be done systematically to choose the best metal oxide with good potential for arsenic removal from water. Previous work has been mostly focused on experimental study, which is time-consuming and expensive. Only a limited number of simulation study has been conducted, which is confined to only several specific adsorbents, such as oxides of iron. There is a need to do research for other metal oxides to evaluate which one is more capable of removing arsenic from water. In this research work, screening of metal oxides was done using Molecular Dynamics and Monte Carlo Simulation. The molecular structures were optimized and sorption calculations were performed at fixed pressure of 100kPa and temperature of 298K to observe the adsorption capability of metal oxides. Al_2O_3 and SnO_2 were found to be good adsorbent for arsenic removal from water with adsorption capacity of 1681.80 g/g and 975.03 g/g respectively. Previously used Al_2O_3 was used as a benchmark for this research and adsorption capacity results also proved it. It was observed that SnO_2 has potential to remove arsenic from water with adsorption capacity 975.03 g/g. The results displayed that SnO_2 can be one of the best adsorbents for application of arsenic removal from water. It is concluded that apart from using conventional metal oxides for arsenic removal, other metal oxides should be studied and can also be used as an adsorbent as they can provide great adsorption capacity for arsenic removal from water.

Introduction

Water is an essential element for living things to thrive. Humans can't survive without water on this planet. However, with the increasing population and industrialization, access to safe drinking water is becoming more difficult. Water contamination has become a global problem. Developing countries are facing even more severe problems in this regard. According to World Health Organization (WHO), 80% of diseases are due to unsafe and polluted water [1]. In particular due to domestic, agricultural, medical, technological applications heavy metals have been widely distributed in our ecosystem, thus, raising concerns for human health and the environment.

Heavy metal ions, such as Cadmium (Cd), Lead (Pb), Mercury (Hg), Arsenic (As), are severe threat to living organisms and metals are harmful for health and their prolonged intake may result in worst consequences [2]. Water treatment is necessary if these metals are present in water.

Among all the heavy metals, arsenic accumulation in groundwater is increasing with time due to human activities and natural phenomenon [3]. Approximately 6.12×10^{10} and 2.380×10^{11} g of arsenic is added into our oceans per annum through soil erosion and leaching respectively [4].

Different processes have been employed for water treatment such as coagulation, adsorption and membrane separation. Adsorption is a very popular and effective method for water treatment. Many adsorbents are used for adsorption process like metal oxides, zeolites etc. Excellent adsorbents have a large area-to-volume ratio to provide maximum adsorption sites for metallic ions [5]. Adsorption is the best method for water treatment and specifically for arsenic removal from water as it is easy in operation and economical with greater efficiency. The removal of arsenic depends on the tendency of the adsorbent to sorb arsenic on its surface. There are a lot of adsorbents that can be used for arsenic removal from water and metal oxides tend to be a better candidate due to their surface area and adsorption capacity [6].

Every metal oxide has a different capacity to sorb a compound to be removed. Some metal oxides like iron oxides and aluminum oxide have been studied by experiments for arsenic removal from water and the experimental studies showed that Fe_2O_3 and Al_2O_3 are good adsorbents [7, 8, 9]. For arsenic removal from water, molecular simulation has evolved as an emerging technology. It has been performed to circumvent limitation of instruments and materials from experimental perspective [10]. Moreover, it provides a platform to study the molecular level interpretation for parameters like energy, enthalphy or entropy [11].

From the review, it is found that although a myriad of experimental work has been available for study of heavy metal removal from water, the investigations using molecular simulation are scarcely available typically for arsenic separation. Among the limited number of studies, they are only confined to specific adsorbents of iron oxide.[12, 13]. There should be research work related to molecular simulation and screening study for arsenic removal from water to select the best adsorbent for arsenic removal from water with good and effective adsorption capacity, it is important to be conducted but has received less scrutiny to date.

In this research work, 11 metal oxides will be studied and adsorption capacity of these adsorbents will be unveiled by adopting Monte Carlo Simulation on Material Studio Software. The metal oxides selected to study for arsenic adsorption are Fe_2O_3, Al_2O_3, TiO_2, ZrO_2, Ag_2O, CaO, CeO_2, La_2O_3, MgO and SnO_2 because of their applications in water treatment [14, 15, 16, 17, 18, 19, 20]. The metal oxides Fe_2O_3 and Al_2O_3 are used as commercial adsorbents for arsenic removal from water and they are included as a benchmark [9] for sorption calculations whereas the other eight metal oxides are studied for sorption loading to remove arsenic from water.

Methodology

The simulation study was performed using Material Studio 8.0 Software [21]. Adsorption phenomenon was studied using molecular dynamics simulation on MS [21]. The geometry optimizations of all the metal oxide structures given in figure 1 was done using the Focite module with a Universal forcefield. Universal force field provides full coverage of the periodic table. It is good for predicting geometry and energy differences of organic molecules, inorganics and metal complexes. This force field corrects the angles and optimize the bond distance of molecules [22]. The structures of metal oxides adsorbents are given in figure 1.

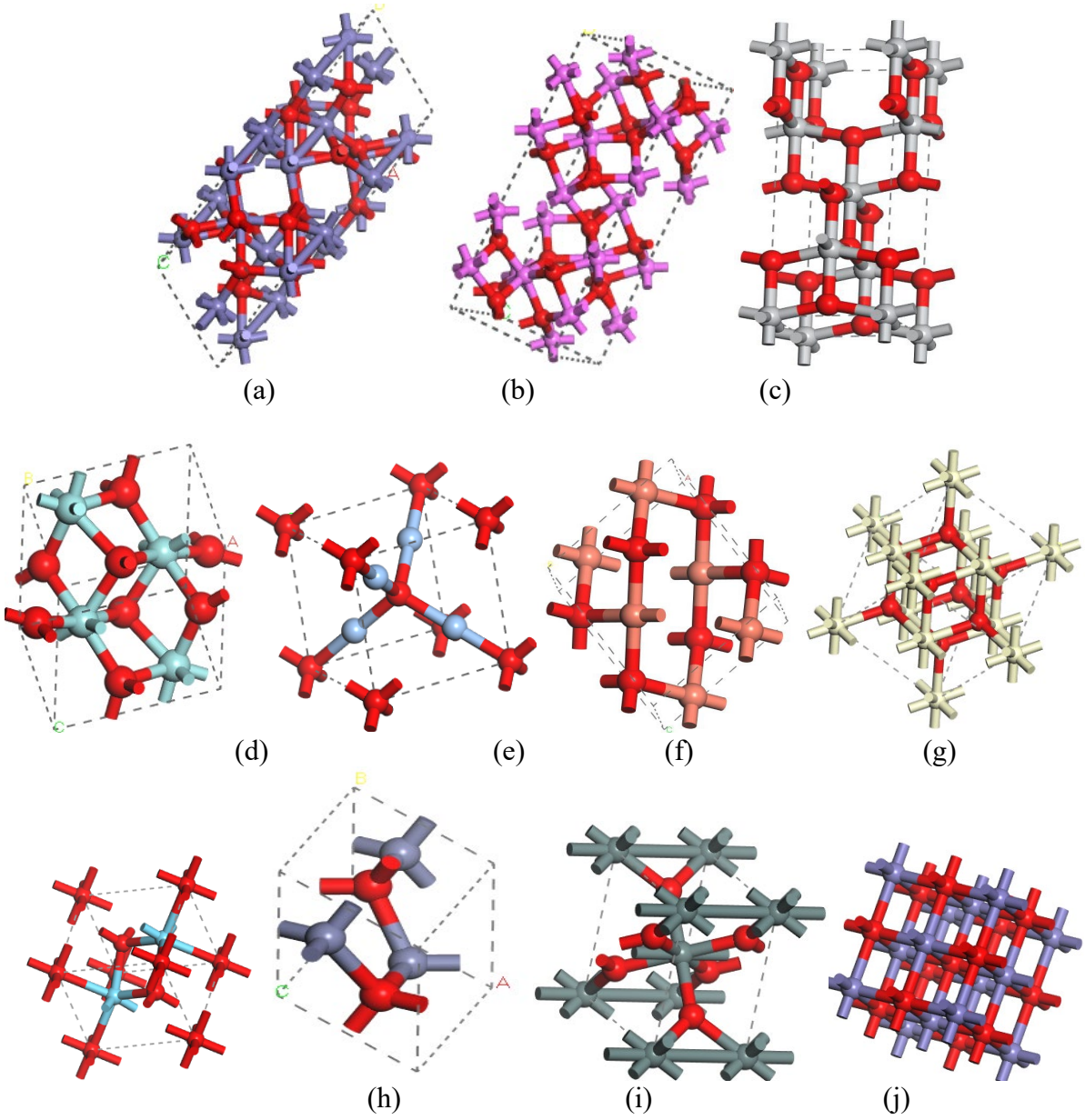

Figure 1: Illustration of adsorbents in Material Studio (a) Fe_2O_3 (b) Al_2O_3 (c) TiO_2 (d)ZrO_2 (e) Ag_2O (f) CuO (g) CeO_2 (h) La_2O_3 (i) ZnO (j) SnO_2 (k) FeO

First of all, selected adsorbents structure was imported from Material Studio library and surface was built for each metal oxide. Then using Forcite module, Geometry Optimization calculations were performed. Geometry optimization was done to achieve stability of structure by energy minimization [23]. After that, sorption calculations were performed using Universal forcefield at temperature 298.0 K. From practical observation, it was seen that most water treatments plants are operated at room temperature and 100kPa, previous simulation studies were also performed at 298.0K [24, 25, 26, 27] and 100kPa [28]. The computations were performed using Monte Carlo Simulation at fixed pressure of 100kPa. This type of simulation is called as Grand Monte Carlo Simulation where temperature is kept constant and pressure is fixed and potential of adsorbent is estimated as sorption loading value [21].

Sorption at fixed pressure task resembles experimental conditions and provides average loading of sorbate component at a given temperature. The Metropolis method was employed using the

Universal forcefield in Materials Studio. The Metropolis method is a conventional Monte Carlo simulation approach that handles the sorbent as rigid structure and solely incorporates sorbate translations and reorientations [21]. Under the Metropolis method, the fixed pressure sorption function, also known as Grand canonical Monte Carlo (GCMC) simulations was used to predict the amount of sorbate at the designated temperature and pressure. It was performed using "Sorption" module in material software with medium quality. The sorption loading value of arsenic within the metal oxide showed its adsorption capacity.

Result and Discussion

The geometery optimization parameters of initial structures (before optimization) and final structure (after performing geometery optimization) for selected metal oxides are given in Table 1. The calculations showed that the total enthalpy of the structure was lowered. This reduction in enthalpy value stabilizes the structure and then it was further used for sorption calculations. The optimization of van der waals energy and non-bond energy are major contributor for optimizing the total energy of the molecular structure [29]. The total molecular structure energy is reduced in this way to acheive stability.

Table 1: Structure parameters of metal oxides before and after Geometry Optimization on Material Studio

Sr. No.	Metal Oxide	Before geometry optimization of stucture parameters	After geometry optimization of structure parameters
		Total Enthalpy (kcal/mol)	Total Enthalpy (kcal/mol)
1	Fe_2O_3	179525.1	158163.3
2	Al_2O_3	501334.3	444405.8
3	TiO_2	9245.8	7144.9
4	ZrO_2	291102.3	80875.7
5	Ag_2O	407.6	217.5
6	CuO	7439.88	5757.75
7	CeO_2	9768.1	9726.7
8	La_2O_3	31471.5	27291.1
9	ZnO	17667.9	17326.5
10	SnO_2	70863.4	67335.6
11	FeO	19802.6	17971.7

Arsenic adsorption result from water using selected metal oxides are shown in table 2. The sorption loading was obtained from sorption module that is further used to calculate adsorption capacity.

Table 2: Sorption Loading and average total energy of metal oxides after loading, result for all selected metal oxides.

Metal Oxide	Average Sorption Loading	Maximum Sorption Loading	Adsorption Capacity (g/g)
Fe_2O_3	0.973	7	13.51
Al_2O_3	81.80	91	1681.80
TiO_2	0.045	2	1.58
ZrO_2	8.82×10^{-3}	2	0.436
Ag_2O	0.083	3	4.05
CuO	0.086	3	5.619
CeO_2	4.4×10^{-4}	1	0.647
La_2O_3	8.04×10^{-3}	3	3.908
ZnO	0.239	3	17.59
SnO_2	14.21	18	975.03
FeO	3.3×10^{-4}	1	1.126

Fe_2O_3, Al_2O_3 were used as a benchmark to compare the sorption loading since they are conventionally used as adsorbent for arsenic removal from water with good adsorption capacity [9, 10]. The adsorption capacity obtained for Fe_2O_3 and Al_2O_3 was 13.51 g/g and 1681.80 g/g respectively, while for SnO_2 the adsorption capacity obtained was 975.03 g/g. It was the second adsorption capacity among all these metal oxides. The arsenic adsorption on SnO_2 is shown in the Figure 2, in which the red dots above the SnO_2 indicates arsenic.

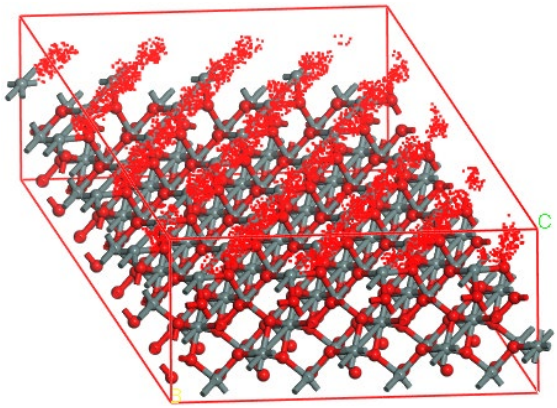

Figure 2: Adsorption of Arsenic on the surface of SnO_2 at fixed pressure

This finding implied that it has a greater tendency to sorb arsenic and has potential to be a good adsorbent to remove arsenic from water. It should be studied as adsorbent for arsenic removal from water. Review from literature suggests that SnO_2 is an effective adsorbent to remove other toxic metals like lead and cadmium [20] since it has the excellent capability and adsorption capacity. It is due to its interesting semiconducting property with band gap of 3.6 eV between O_2 and Sn that give great capability of heavy metal ions removal [20]. Moreover, according to literature SnO_2

nano-particles have high surface area of 128 m^2/g [30] which makes it good adosrbent with great efficiency while microporous Fe_2O_3 has 111m^2/g [31] that is less than SnO_2surface area.

Conclusion

The screening of different metal oxides for arsenic removal from water was done using Material studio software and sorption calculations were performed. The adsorbents according to sorption capacity value were in the order of: $Al_2O_3 > SnO_2 > ZnO_2 > Fe_2O_3 > CuO > Ag_2O > La_2O_3 > TiO_2$ $FeO > CeO_2 > ZrO_2$. The results obtained from this present research work showed that among above 11 chosen metal oxides, SnO_2 has second adsorption capacity of 975.03 g/g. Al_2O_3 has the maximum adsorption capacity of 1681.80 g/g among all and has been used previously for arsenic removal while Fe_2O_3 had adsorption capacity of 13.51g/g that is less than SnO_2. SnO_2 is a metal oxide that had not been used for arsenic removal from water but is used to remove other toxic metals like cadmium and lead from water. This study suggests that SnO_2 has good adsorption capacity and potential to remove arsenic from water and should be explored as an adsorbent to remove arsenic from water. Moreover, that other metal oxides like CuO, MnO, ZnO and FeO should also be studied for arsenic removal form water. The effect of operating variables towards adsorption capacity should also be studied in the future to optimize the separation performance.

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