

Adsorption of Propazine, Simazine and Bisphenol A on the Surface of Nanoparticles of Iron Oxide Nanoparticles of Carbon and Metallic Oxides

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Abstract

Simazine and propazine are selective triazine herbicides currently in use to control broad-leaved weeds and annual grasses around the world. Bisphenol A (BPA) is an industrial chemical used in the production of polycarbonate plastics often found in consumer goods, such as plastic containers, baby bottles etc. These synthetic compounds are known to increase the risk of cancer, cause adverse reproductive effect in reptiles, mammals, birds, humans, and lead to other health problems. They have become some of the principal agents of contamination in water bodies around the world through herbicide runoff, industrial waste and leaching. Some triazines such as atrazine are banned in most European countries for over ten years due to their adverse reproductive effect in mammals, birds and humans; however propazine and simazine are still in use around the world. The removal of these compounds from contaminated water is an exigent challenge. In this study, we investigated their affinity for the surface of nanoparticles (NPS) and standard metallic oxides in an effort to exploit the unique potential applications of NPS for water purification systems. We studied the adsorption of the two triazines and BPA on the surface of NPS of iron (III) oxide, NPS of carbon, bulk iron (III) oxide and aluminum oxide at pH 6 and pH 8 using UV-Visible spectroscopy. Result indicates that these compounds have different affinity towards the surface of metallic oxides and carbon at various pHs. In general, there is relatively high adsorption of some of these compounds on the surface of NPS compared to bulk particles. NPS of carbon have shown the highest affinity for all the three compounds. The lower pH was found to be favorable for all of the compounds except for BPA. BPA have shown high adsorption at pH 8 than at pH 6.

Keywords

Triazine, Adsorption of Nanoparticles, Nanoparticles of Iron Oxide, Nanoparticles of Carbon, Bisphenol A

1. Introduction

Surface, ground and drinking water contamination by various synthetic chemicals such as herbicides, pesticides, insecticides as well as other industrial chemicals has been a major problem throughout the world [1]-[10]. Especially as the need to grow more food increases, it becomes necessary to use more of these chemicals to increase output of food production. Millions of tons of these products are being used every year leading to an elevated level of contamination of water bodies through agricultural runoff and industrial effluent. Triazines are wide-spectrum pesticides used to control broad-leaved weeds and annual grassy weeds. Some triazines such as atrazine are banned in most European countries for more than ten years due to their presence in water system at high concentration which may have adverse reproductive effect in mammals, birds and humans. Triazines such as propazine and simazine are currently in use around the world. Various studies have shown triazines to be risk factors for different forms of cancers. Consuming high doses over long periods of time caused tremors, damage to the testes, kidneys, liver and thyroid and a decrease in sperm production in lab animals [11]-[24]. Bisphenol A (4,4'-(propane-2,2-diyl)diphenol) (BPA) is a well know synthetic compound that is used in the production of plastic containers such as food and beverage containers, baby bottles, water bottles, medical devises, baby toys and many other consumer products [25]. BPA is a source of water contamination that is known to enter water systems through leaching, direct waste disposal of consumer goods and from industrial waste. It has been detected in ground water, surface and drinking water [26] [27] [28] [29] [30]. It is a known endocrine disruptor and has been implicated in various adverse reproductive effects in birds, frogs, reptiles, fish and mammals. It has been linked to prostate, breast cancer, birth defects, miscarriages, and many other conditions [31]-[43]. The removal of these compounds from contaminated water has become a challenge and needs a unique approach. Studies have shown these environmental contaminants interact with the surface of materials, such as quartz, calcite, kaolinite, alumina, organic compost and nanoparticles, moreover these studies highlighted the potential use of these materials as environmental remediation [44] [45] [46] [47] [48]. Particles with the size range of 1 nm to 100 nm are called nanoparticles (NPS). They possess enhanced or altered physical, chemical and biological properties which make them superior in different applications than bulk particles. Correspondingly, there has been a dramatic increase in emerging new uses of NPS for various applications, including; medicine, biotechnology, antimicrobial activities, food, beverages, chemicals, communications,

consumer goods and environmental remediation [49] [50] [51] [52] [53]. In this study, we investigated adsorption of simazine, propazine and BPA on the surface of NPS of iron (III) oxide, NPS of carbon, bulk iron (III) oxide and aluminum oxide. The effort is to exploit NPS' unique properties that can potentially be applied in water purification systems. In order to achieve these goal adsorption batch experiments were performed with 0.4 g/L of NPS of Fe₂O₃, NPS of carbon, regular Fe₂O₃, or regular Al₂O₃ at pH 6 and pH 8 and UV-Visible spectroscopy was used to determine surface adsorption.

2. Materials and Experimental Methods

2.1. Materials

The two triazine herbicides, simazine and propazine and bisphenol A (**Figure 1**), iron (III) oxide Nanopowder, carbon nanopowder, aluminum oxide, and iron (III) oxide are all purchased from Sigma-Aldrich chemical company (St. Louis, MO). All chemicals used for this experiment were reagent grade. Spectronic GENESYS spectrophotometer from Thermo Electron Corporation (Madison, WI), New Brunswick I24 Bench top Incubator Shaker from VWR (Radnor, PA) and Fisher Marathon 26 KMR Centrifuge were used.

2.2. Adsorption of Selective Triazine Herbicides and Bisphenol A on the Surface of Carbon Nanoparticles, Metallic Oxides and Nanoparticles of Metallic Oxides as Monitored by UV-Vis Spectroscopy

Stock solution with appropriate concentration of the contaminants such as simazine, propazine and bisphenol A were prepared. Stock solution of iron (III) oxide, nanoparticles of iron (III) oxide, aluminum oxide, and nanoparticles of carbon were prepared to give a concentration of 0.4 g/L. Appropriate sample concentration was run in an UV-Visible spectrophotometer and the maximum

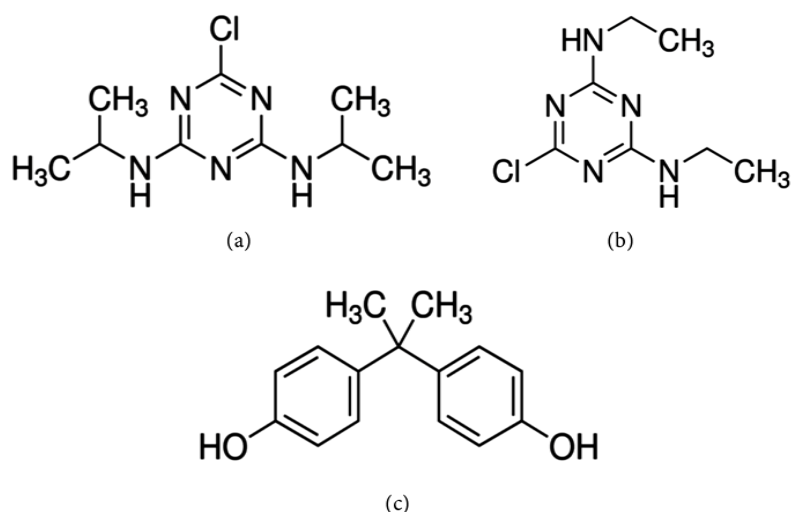


Figure 1. Chemical structure of Triazine herbicides and Bisphenol A: (a) Propazine, (b) Simazine and (c) Bisphenol A.

absorption wavelength for simazine, propazine and bisphenol A were determined to be 227 nm, 222 nm, and 285 nm respectively. Once the maximum absorption wavelength was determined for the individual contaminant, ten standard samples with concentrations from 10 - 160 μM of contaminant were placed in an UV spectrophotometer to obtain standard curve for each individual samples. The standard curve was used to determine the adsorbed amount of adsorbates on the surface of the adsorbent. In each experiment, various ranges of concentrations of the individual contaminant was placed in an Erlenmeyer Flasks, and 10 ml adsorbent solution (Fe_2O_3 , Al_2O_3 , Fe_2O_3 nanoparticles, or carbon nanoparticles) at either pH 6 or pH 8; was added to each flask. The samples were placed in a shaker at room temperature for 17 hours and agitated with a speed of 170 rpm. In order to minimize photolytic activity, samples were left overnight in the incubator with no direct light. After 17 hours, the samples were centrifuged at 1000 rpm for 15 minutes at room temperature and filtered with the help of vacuum filtration. After filtration, the UV absorption of each sample was measured at appropriate wavelength (for simazine, propazine and bisphenol A 227 nm, 222 nm, and 285 nm respectively) with distilled water as baseline. Once the absorbance data was collected, it was used to determine the final concentration of the respective contaminants by using the equations derived from the standard curves; $y = ax + b$. Where, y is absorbance, a is concentration and b is a constant. The amount of adsorbed contaminant per gram of adsorbent was calculated as the difference between the initial concentration and the concentration at equilibrium using the equation; $q = (C_o - C_e)(M)V/m$. Where Q is the amount adsorbed molecule (mg/g). C_o is the initial concentration, C_e is the concentration at equilibrium, V is the volume of working solution, M is the Molar Mass of contaminant and m is the mass of adsorbent added to the working solution. Weight in mg of respective contaminant/g of adsorbent versus concentration (mM) or (μM) were plotted to show the extent of binding.

3. Results and Discussion

Synthetic compounds, simazine, propazine and bisphenol A were used to study adsorption on the surface of adsorbent compounds, NPS of iron (III) oxide, NPS of carbon, bulk iron (III) oxide and aluminum oxide. **Figure 2** shows the plot of surface coverage vs. concentration for adsorption of BPA on the surface of various adsorbent. BPA have been found to shown the highest bidding on the surface of carbon NPS at pH 6 followed by aluminum oxide, iron (III) oxide and NPS of iron (III) oxide respectively. In **Figure 3**, the same trend was observed at pH 8 for carbon NPS, aluminum oxide, while the NPS of iron (III) oxide showed higher surface adsorption than bulk iron (III) oxide. Moreover, the entire compound tested shown to have higher surface coverage by BPA at pH 8 than at pH 6. These phenomena could be explained based on the charge that can be developed on BPA due to the increase in pH. The pKa value for BPA is 9.9, as the pH gets closer to the pKa value more of the BPA exists as negatively charged ion and

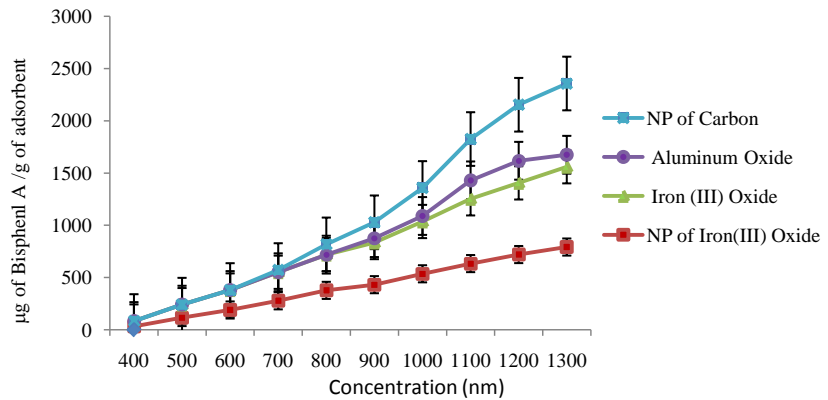


Figure 2. Plot of surface coverage vs. concentration for adsorption of bisphenol A on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 6.

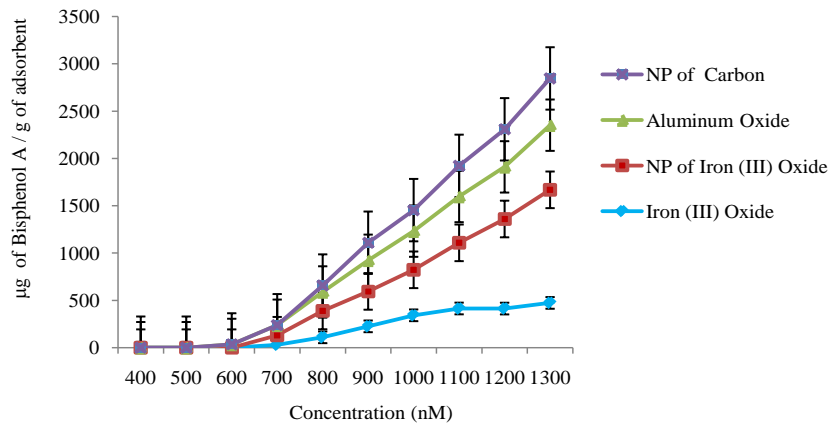


Figure 3. Plot of surface coverage vs. concentration for adsorption of bisphenol A on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 8.

this allows better interaction with the surface of the adsorbent. **Figure 4** and **Figure 5** show adsorption of propazine on the surface of all the adsorbents tested. Propazine has the highest adsorption on the surface of carbon NPS followed by NPS of iron (III) oxide, aluminum oxide and NPS of iron (III) oxide at both pH 6 and pH 8. The same trend can be seen for simazine at both pH 6 and 8, only in this case the adsorption on the surface of aluminum is better than NPS of iron (III) oxide and iron (III) oxide (**Figure 6** and **Figure 7**). In general, NPS expected to have more reaction site available for the interaction due to large surface area to mass ratio and this may explain why we see better surface coverage on NPS than the corresponding bulk particles. The fact that there were relatively higher adsorption on the surface of metallic oxides at pH 6 than at pH 8 can be explained due to the increase in the number of adsorption sites on the surface of metallic oxides at lower pH compared to higher pH, *i.e.* more of $M-OH_2^+$ presents at pH 6 and more of $M-OH$ presents at pH 8. Charge distributions on the surface of metallic oxides are shown below at higher and lower pHs).

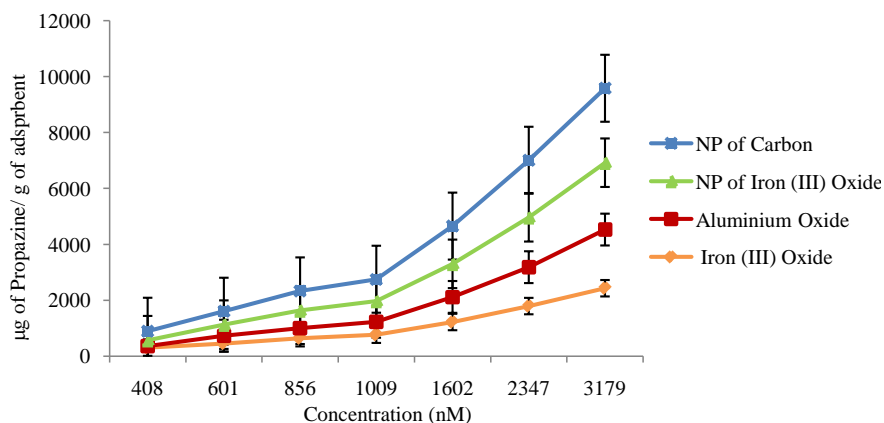
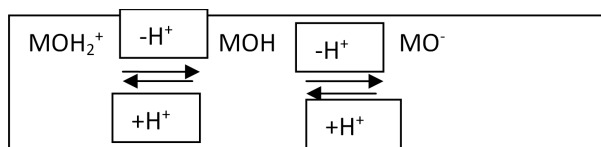


Figure 4. Plot of surface coverage vs. concentration for adsorption of propazine on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 6.

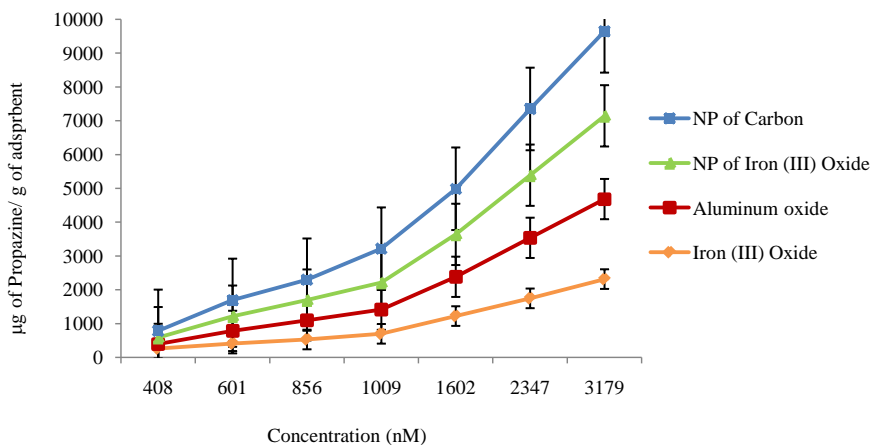


Figure 5. Plot of surface coverage vs. concentration for adsorption of propazine on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 8.

4. Conclusion

The adsorption properties of metallic oxides depend on the charge, surface area, pore-size and characteristics of the surface. In general, adsorption on surface of metallic oxides can be explained using two mechanisms. The first is availability of adsorption site and the second mechanism is electrostatic attraction due to surface charge. At a lower pH surface of metallic oxide expected to have more available reaction site. However, our result shows favorable adsorption of BPA at the higher pH. This may be an indication that the charge developed on the BPA plays a major role in creating electrostatic interaction than the available binding

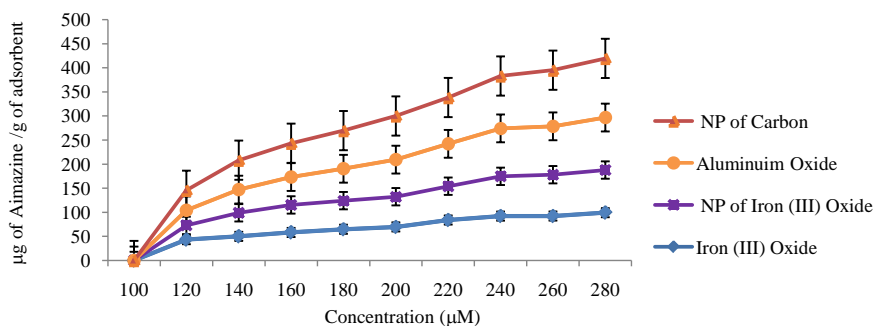


Figure 6. Plot of surface coverage vs. concentration for adsorption of simazine on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 6.

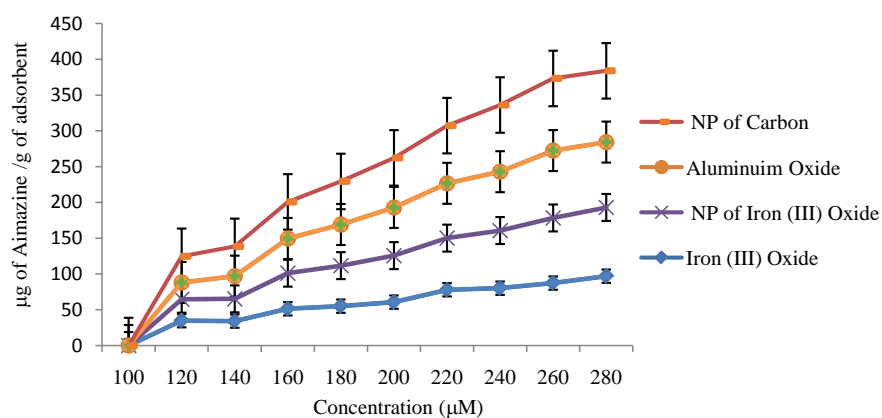


Figure 7. Plot of surface coverage vs. concentration for adsorption of simazine on the surface of NPS of iron (III) oxide, NPS of carbon, regular iron (III) oxide, and aluminum oxide at pH 8.

site on the surface of metallic oxides that could be developed at a lower pH. For propazine and simazine, adsorption capacity and affinity increased at pH 6 which is consistent with the increase in the available reaction site on the surface of metallic oxides at lower pH than at higher pH. On the other hand, NPS of carbon found to be the best adsorbent of all the compounds tested at both pHs. In this case, it could be because that the unique properties of NPS are at play, *i.e.* the large surface area to mass ratio for NPS compared to the bulk particles. In general, NPS have shown to have better adsorption for the compound tested, moreover we have shown that pH of the solution could affect the interaction. Future study that includes various reaction conditions, such as ionic strength and presence of multiple adsorbent and adsorbates could provide more information about the interaction and open up ways in using NPS for water purification systems.

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