

Porous ceramic modified with hydrous manganese oxide as potential sorbent of cadmium and lead in water

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Abstract

Hydrous manganese oxide (HMO) is capable of adsorbing heavy metals in water, specifically cadmium and lead. HMO was integrated into porous ceramic water filter using 3-aminotriethoxysilane (APTES) as a coupling agent. Three porous ceramic samples, one modified with HMO using APTES, another modified with HMO without APTES, and one unmodified porous ceramic, were viewed under a JEOL JSM-5510LV model Scanning Electron Microscope to view their external morphological structures. Images show that porous ceramic modified with HMO using APTES have serrated bulb-like structures compared to the amorphous covering exhibited by the porous ceramic modified with HMO only. The porous ceramic modified with HMO was then exposed to cadmium and lead solutions of known concentrations. The amount of the heavy metals in the solution was then quantified using Agilent Microwave Plasma-Atomic Emission Spectrometer system. The analysis shows that porous ceramic modified with HMO using APTES results to lower amounts of cadmium and lead in water samples compared to porous ceramic only.

Keywords: *heavy metals, porous ceramic, hydrous manganese oxide, lead, cadmium*

Introduction. The removal of heavy metals has been a subject for research [1,2,3] due to the pressing issue of the presence of heavy metals at hazardous levels in several bodies of water around the world [4,5,6,7,8,9]. This is a subject for concern, for heavy metals have been established to have adverse effects both to the human body [10] and to the environment [11]. Meanwhile, among these toxic heavy metals, lead and cadmium are two of the most commonly detected.

There are several methods that effectively remove heavy metals from water such as chemical precipitation, ion exchange, and electrochemical removal. However, these said methods for filtering industrial waste water can discharge harmful secondary wastes [12]. Nowadays, technology shifts to creating sorbents that can adsorb heavy metals from water [1,13].

Natural materials and biological wastes were used as heavy metals sorbents [1,13,14] that can adsorb heavy metals such as, but not limited to, cadmium and lead. However, it is notable that these biological wastes and natural-occurring materials needed additional modification in order to effectively adsorb heavy metals. These modifications allow the materials to incorporate functional groups, specifically hydroxyl, carbonyl, and epoxy groups [1] which serves as additional adsorptive sites to the surface of the material [13].

In addition to sorbents mentioned above, different metal oxides were also used as inorganic sorbents for heavy metals in water [3,15]. Among these metal oxides, HMO is the only one capable of adsorbing both cadmium and lead at the same time.

The metal oxides adsorb heavy metals in water

by ion-exchange method [16]. The heavy metals are attached to the metal oxides by electrostatic attractions. The oxides act as nucleophiles to attract the positively charged heavy metal ions. This nucleophilic attack is also utilized by the biological sorbents. However, these sorbents use the oxygen containing functional groups as the nucleophiles to adsorb the heavy metal ions [13].

It is notable that all of these metal oxides mentioned, including HMO, were used as is to adsorb heavy metals. These metal oxide particles, in their colloidal form, were suspended in the heavy metal solution and were allowed to interact with the heavy metal ions. HMO particles were indeed utilized for the adsorption of cadmium and lead [15]; however, they did not provide an actual medium for HMO to be used in a practical setting. This is significant because HMO is in the form of particles, which, when dispersed in water contaminated with heavy metals, is difficult to recover.

However, these particles can also be incorporated into other matrices or composites as a medium to hold the metal oxides particles. Hydrous manganese oxide particles were incorporated into a water retaining polymer which retains water for the plants while filtering cadmium ions in interstitial water around the roots [13]. In the same way, a ceramic membrane was coated with chitosan nanoparticles which has improved the uptake of nickel ions in water [18]. Silver nanoparticles were attached to a porous ceramic which serves as a medium to hold the silver nanoparticles, for antibacterial purposes [19]. This is to induce an antibacterial effect on the ceramic, rather than just physically filtering the microorganism without killing it.

Only Lv et al. [19] have used 3-aminopropyltriethoxysilane (APTES), an organic coupling agent to attach the metal nanoparticles to the ceramic, which are both inorganic in nature. In the case of Peng et al. [17], the medium where the hydrous manganese oxide was attached was an organic polymer. This is also applicable for Chooaksorn and Nitorisavut [18], yet in their case, it is chitosan particles that are the organic material. Lv et al. [19] used APTES as a coupling agent as it forms Si-O-Si bonds between the silver nanoparticles and the silicone-based ceramic. Since previous research have indicated that HMO can remove lead and cadmium from water, and porous ceramic can be used as a medium when 3-(aminopropyl)triethoxysilane (APTES) is used as a coupling agent.

In terms of effectivity, it is notable that HMO is effective in adsorbing heavy metals in water. Gadde and Laitinen [15] observed that 0.2 mole heavy metal ion (cadmium, tellurium, zinc) was adsorbed per mole HMO and 0.56 mole of lead ions was adsorbed per mole HMO. Peng et al. [17] stated that poly(acrylamide-co-sodium acrylate) impregnated with HMO can absorb cadmium ions on average of 735 mg/g. Furthermore, it is stated that the polymer with HMO can adsorb cadmium ions up to 135% times higher than the polymer without any HMO. These findings are essential to the present study because it can provide a groundwork in the comparison of the activity of the ceramic modified with HMO and the ceramic without HMO in adsorbing cadmium and lead heavy metal ions.

The relative roughness of the surface is a factor to consider on adsorption of heavy metals. A rougher surface is often attributed to more active adsorptive sites on the surface. Aziz et al. [14] described that limestone and crushed bricks are able to adsorb 90% and 80% of the heavy metals, respectively, which is attributed to the roughness of the media. In the same way, Chooaksorn and Nitorisavut [18] were able to infer that the more chitosan nanoparticles were loaded to the ceramic membrane, the smoother the surface became, and the adsorptive capabilities decreased. A rougher surface would also equate to a higher surface area, which can also be achieved by decreasing the size of the metal oxides into nanoparticles [5].

It is expected that the resulting HMO-porous ceramic composite will be able to remove a significant amount of lead and cadmium compared to regular porous ceramic. The results of this study may prove important to subsequent research about heavy metal removal from water. While Gadde and Laitinen [15] showed that HMO can be used to remove lead and cadmium from water, this study may provide the foundation for future research into the practical use of HMO in heavy metal removal.

This study aims to determine whether HMO remains capable of removing cadmium and lead from water when attached to porous ceramic using APTES. It specifically aims:

- (i) To determine whether HMO can be attached to porous ceramic using APTES;

- (ii) To measure the amount of cadmium and lead (in mg) in water samples after treatment with (a) porous ceramic, and (b) HMO-porous ceramic composite;

- (iii) To compare the amount of cadmium and lead (in mg) in water samples after treatment with (a) porous ceramic, and (b) HMO-porous ceramic composite.

Methods. The methods used in this study were adapted from Lv et al. [19] and Gadde and Laitinen [15]. The method used in the preparation of the HMO colloidal solution was that of Gadde and Laitinen's [15]. The method Lv et al. [19] used in attaching the metal oxide to the porous ceramic using APTES was modified –using HMO particles instead of silver nanoparticles.

Preparation of HMO-Porous Ceramic Composites. Hydrous manganese oxide (HMO) was synthesized by slowly adding 60 mL 0.5 M MnCl_2 solution to alkaline permanganate solution, which consists of 40 mL 0.5 M KMnO_4 mixed with 40 mL 1.0 M NaOH. Additional HMO colloidal solution would be synthesized with the mole ratio 3:2:4 of MnCl_2 , KMnO_4 , and NaOH respectively. Porous ceramic pieces were soaked in gently boiling piranha solution (3:1, v/v, 95% H_2SO_4 /30% H_2O_2) for 20 minutes, then rinsed by soaking in triple-distilled water for 24 hours. The porous ceramic samples were then preheated at 200°C in a BINDER FD Series Heating Oven for 2 hours with 15-minute cooling down in a desiccator after the first hour. After preheating, the porous ceramic pieces were cooled down for 30 minutes. These were then soaked in 1% APTES-ethanol solution for 30 minutes at ambient temperature. The pH of the solution was adjusted to 3.5-5.5 by adding aqueous CH_3COOH drop-wise. The pieces were then cured in the same heating oven at 100°C for 4 hours to allow the APTES to fully condense into the ceramic. Finally, the porous ceramic with APTES was immersed for 24 hours in the HMO colloidal solution. Unattached HMO was subsequently rinsed off of the porous ceramic using 95% ethanol.

SEM Analysis. The morphology of the prepared HMO-porous ceramic composites was analyzed at 250x and 1000x magnification through JEOL JSM-5510LV scanning electron microscope (SEM) at the Southeast Asian Fisheries Development Center (SEAFDEC) at Tigbauan, Iloilo. These were compared to the morphology of control samples of porous ceramic that did not undergo the modification process as well as porous ceramic soaked in HMO for 24 hours without APTES, which were also analyzed using SEM at SEAFDEC. Photomicrographs of treatment and control set-ups from SEM analysis were obtained.

Experimentation. For experimentation, six HMO-porous ceramic composites were prepared along with six porous ceramic controls. Cadmium and lead solutions (approximately 100 mg/L) were prepared using 1000 mg/L standard solutions diluted with distilled water. One HMO-porous ceramic composite was suspended in a beaker containing 50 mL heavy metal solution (one each for cadmium and

Table 1. Amounts of cadmium and lead in water samples without treatment, after treatment with porous ceramic, and after treatment with HMO-porous ceramic composite.

Treatment	Amount of cadmium (mg)		Amount of lead (mg)	
	Porous ceramic	HMO-porous ceramic composite	Porous ceramic	HMO-porous ceramic composite
Mean \pm S.D.	5.3020 \pm 0.0632	5.1905 \pm 0.0346	4.6937 \pm 0.1022	4.1728 \pm 0.1052
p-value	0.0276		0.0018	

lead) for three hours. The solutions were agitated using a laboratory shaker during the whole period.

The same set-up was also applied for the porous ceramic controls. Each set-up was performed in triplicate.

MP-AES Analysis. The concentration of cadmium and lead in water samples were measured using Agilent Microwave Plasma-Atomic Emission Spectrometer (MP-AES) system at the Department of Science and Technology Region VI. Standard MP-AES procedure was performed on all six samples of cadmium solution and six samples of lead solution. Concentrations, in ppm, were obtained after the MP-AES procedure.

Data Analysis. To compute the amount of heavy metal in mg in each of the heavy metal solutions, the concentration obtained from the MP-AES analysis in ppm was multiplied by the volume of the solution in liters. One-tailed t-test for two independent means at 95% confidence interval was used for the final heavy metal amounts computed. The corresponding means and standard deviations of replicate measurements were calculated.

Waste Disposal. Proper disposal of all reagents was observed. Cadmium and lead solutions was placed in separate containers then turned over to the University of San Agustin for disposal. Piranha solution was discarded in the sink with copious amounts of water after cooling and neutralization. Other chemicals such as HMO colloidal solution were placed in separate containers then turned over to the PSHS-WVC SRS for disposal.

Safety Procedure. All parts of the methods were performed with the proper laboratory gear, including laboratory gowns, latex gloves, and face masks, to avoid any injury related to spillage of and fumes from the chemicals used. Insulated gloves were also used in performing the laboratory oven procedure. The heavy metal samples were stored in amber bottles, sealed, and tightly packed when transported for MP-AES analysis to avoid breakage and spillage. First-aid kits were readily available during all parts of the procedure, and responsible adults were on-call if any serious harm were to come upon any of the persons involved. However, the entire conduct of the methods did not result to any such harm or injury.

Results and Discussion. HMO-porous ceramic composites were prepared by attaching HMO to porous ceramic pieces using APTES as a coupling agent; then, they were observed, along with porous ceramic that did not undergo the modification process as well as porous ceramic soaked in HMO without APTES, under the scanning electron

microscope (SEM) to note the differences in their surface morphology. HMO-porous ceramic composites and porous ceramic controls were used for experimentation by soaking them in cadmium and lead solutions for three hours. The amounts of cadmium and lead before and after were determined through the concentrations obtained from microwave plasma-atomic emission spectrometry (MP-AES) analysis.

SEM Photomicrographs. The attachment of HMO to porous ceramic through APTES was examined using the SEM. Photomicrographs of the surfaces of porous ceramic, porous ceramic with HMO, and porous ceramic with APTES and HMO were taken at 250x (Plates 1, 2, and 3) and 1000x magnification (Plates 4, 5, and 6).

For the porous ceramic that did not undergo the modification process, its surface showed a jagged, flaky texture (Plates 1 and 4). On the other hand, the porous ceramic soaked in HMO solution for 24 hours presented a smooth surface, covered in an amorphous substance (Plates 2 and 5). The porous ceramic that underwent the full modification process, which included APTES and HMO, appeared to have a rougher texture than the previous two control samples, and there is a presence of serrated bulb-like structures on the surface as well (Plates 3 and 6).

After SEM analysis, only the porous ceramic modified with HMO using APTES exhibited morphological structures characteristic of HMO, when compared with the porous ceramic control and the porous ceramic treated with HMO only. While the porous ceramic control presented a rough surface, it was not similar to the morphology of HMO; likewise, the porous ceramic treated with HMO only presented a smoother surface, which is not similar to the rough surface expected of HMO.

The texture of the first porous ceramic control, which was subjected to neither HMO nor APTES, under the SEM, which appeared to be rough and have disc-like structures around 30 μm wide, was different from that of the results of Lv et al. [19], which showed a consistent, flat surface with uniformly distributed pores. This implies that the porous ceramic used by Lv et al. [19] was different from that used in this study.

Zandvakili and Ranjbar [23], whose study involved forming a composite from poly vinylidene fluoride (PVDF) and HMO, show that their HMO samples as well as the produced composites from PVDF and HMO both appear to have rough surfaces under the SEM. Gotic et al. [20] studied the microstructures of different manganese oxide particles; the MnO_2 samples in the study also presented rough, serrated surfaces formed

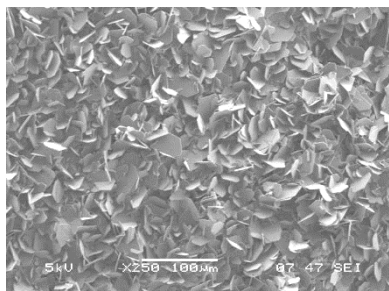


Plate 1. Porous Ceramic (250x)

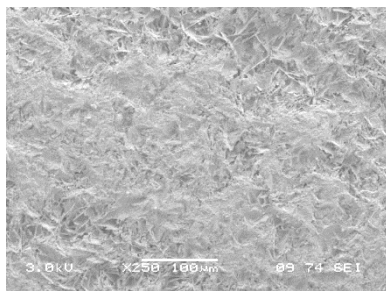


Plate 2. Porous Ceramic with HMO (250x)

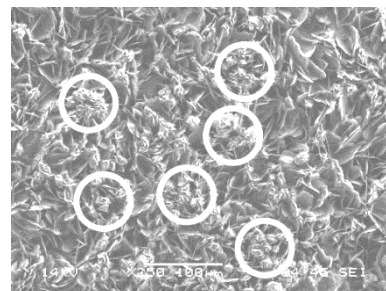


Plate 3. Porous Ceramic with APTES and HMO (250x)

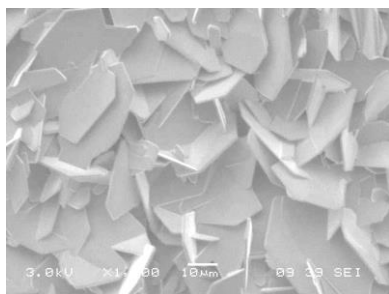


Plate 4. Porous ceramic (1000x)

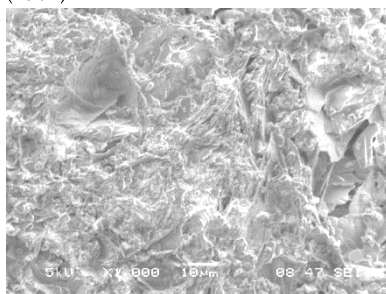


Plate 5. Porous Ceramic with HMO (1000x)

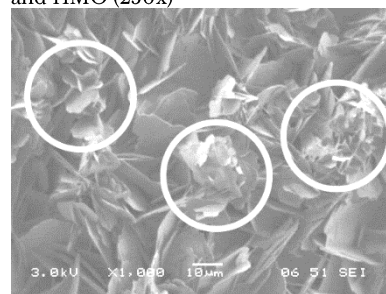


Plate 6. Porous Ceramic with APTES and HMO (1000x)

by nanorods and microparticles. The study of Xiao et al. [22], which produced a composite constituted by poly(vinyl chloride) (PVC) and MnO_2 , resulted to the PVC- MnO_2 composites having rough surfaces as shown in SEM images.

The second porous ceramic control, although exposed to HMO, exhibited a smooth surface, while the first porous ceramic control, which was not exposed to HMO, exhibited a rough surface on its own that differed in appearance from the HMO-porous ceramic composite. Among the three porous ceramic samples in the present study, the HMO-porous ceramic composite was the one which most resembled previous studies' results regarding the appearance of HMO or MnO_2 both in itself and as part of a composite, compared to the two porous ceramic controls, especially in terms of roughness and present structures. After comparison with the results from other studies, the SEM photomicrographs of the samples indicate that HMO was able to attach to porous ceramic through APTES, but not without APTES, denoting the success as well as the necessity of APTES as a coupling agent between HMO and porous ceramic.

Heavy metal amounts. The concentrations of cadmium and lead in the water samples were measured using MP-AES analysis. Using these data, the amounts of cadmium and lead (in mg) in the water samples were then computed. These data are shown in Table 1. Using these data, the amounts of cadmium and lead (in mg) in the water samples were then computed.

After conducting a one-tailed t-test ($\alpha=0.05$) on the cadmium amounts, a p-value of 0.0276 resulted. Since $p < 0.05$, there is enough evidence to support that the water treated with HMO-porous ceramic composite has significantly lower amounts of cadmium than the water treated with porous ceramic only.

The lead amounts also underwent similar statistical analysis, resulting to a p-value of 0.0018. With $p < 0.05$, the water treated with HMO-porous ceramic composite also has significantly lower amounts of lead than the water treated with porous ceramic only. Results of the statistical analysis show that water samples treated with HMO-porous ceramic composite have significantly smaller amounts of heavy metal compared to water samples treated with porous ceramic only. Therefore, the amounts of cadmium and lead in the water samples treated with HMO-porous ceramic composite were significantly lower than those treated with porous ceramic only. It can be then inferred that the HMO in the HMO-porous ceramic composite was able to remove a significant amount of cadmium and lead from the water samples.

Such data agrees with the results of Gadde and Laitinen [15], whose study showed that HMO can adsorb cadmium and lead in aqueous solutions. Their study also was able to show that HMO adsorbs lead in a greater capacity than it adsorbs cadmium. The data above show that the difference between the amount of lead in the water samples treated with porous ceramic and those treated with HMO-porous ceramic composites was bigger than the difference in the cadmium amounts, behaving as predicted by Gadde and Laitinen [15].

However, their study also shows that HMO was able to remove almost all (99.9%) of the lead in their water samples, the concentrations of which are even higher than that used in the present study. The results presented above show that while the HMO-porous ceramic composite was able to remove a significant amount of lead, the difference was not close to 100% as demonstrated by Gadde and Laitinen [15]. This discrepancy can be explained by the difference in the medium; while their study used HMO in its colloidal form, the present study utilizes HMO attached to porous ceramic. The amounts of HMO they used

must be significantly higher than the amount of HMO that was able to attach to the surface of the porous ceramic. It is still clear, however, that both were still able to remove lead from water. In summary, the results regarding the amounts of cadmium and lead in the water samples treated with porous ceramic only and with HMO-porous ceramic show that there is significantly less cadmium and lead in the water samples treated with HMO-porous ceramic than those treated with porous ceramic only. This result supports and is supported by the study of Gadde and Laitinen [15], but with differences that could be accounted for by the change in medium from HMO colloidal solution to HMO-porous ceramic composite. The results suggest that HMO, when attached to porous ceramic using APTES, retains its capability, or part of its capability, in removing a significant amount of cadmium and lead from water.

Error Analysis. SEM analysis showed the morphology of porous ceramic that was different from what was expected. Results were not similar to porous ceramic morphology results of other studies. However, this can be a result of different sources of porous ceramic which can lead to different surface morphologies, and is not a factor in the internal consistency of the study.

MP-AES analysis resulted to concentrations that were different to the expected values. Cadmium and lead solutions were prepared to be 100 mg/L; however, cadmium solutions resulted to values greater than 100 mg/L, while lead solutions resulted to values less than 100 mg/L. This is most likely a result of a deviation in the standard solutions provided. While the standard solutions requested were intended to be 50 mL of 1000 mg/L solutions, neither the volume nor the concentration of these solutions was confirmed. A greater volume or higher concentration can explain the higher values in the cadmium solutions, while a smaller volume or lower concentration may be the cause of the lower values in the lead solutions.

Conclusion. HMO-porous ceramic composites cannot be prepared without a coupling agent; as such, APTES, as a coupling agent, is capable of attaching HMO to porous ceramic to produce HMO-porous ceramic composites. SEM photomicrographs show that porous ceramic treated with HMO only lack HMO characteristic features, but such morphological structures are present in the surface of porous ceramic modified with HMO using APTES.

When treated with HMO-porous ceramic composite, water samples exhibit significantly lower amounts of cadmium and lead compared to water samples treated with porous ceramic only. Statistical analysis of the heavy metal amounts in the treated samples support the expectation of lower heavy metal amounts when treated with the modification of HMO. This confirms that HMO is still able remove cadmium and lead from water even when attached to porous ceramic.

Recommendations. To better understand the attachment of the HMO to the porous ceramic using APTES, it is recommended that future studies

investigating similar phenomenon not only use SEM analysis, but other methods of analysis as well, such as transmission electron microscopy (TEM), Fourier-transform infrared (FTIR) spectroscopy, and X-ray diffraction.

Also, to gain a more in-depth view at the mechanism involving the adsorption of heavy metals using HMO-porous ceramic composites, future studies are recommended to utilize adsorption studies such as adsorption curves, which can visualize the entire process effectively, rather than just final amounts. It may also be beneficial to follow through with the original objectives of the present study, which intended to calculate the percent of heavy metals removed from the water. In any case, it is recommended that all the samples be properly handled and all variables, such as the amount of nitric acid added to the samples, should be controlled to prevent anomalous data.

Further studies also need to be conducted to improve the efficiency of HMO-porous ceramic composite in removing cadmium and lead, especially addressing the reduced surface area-to-volume ratio. It may also be beneficial to conduct further studies at lower concentrations, such as 1.0, 20.0, and 50.0 mg/L, similar to Afkhami et al. [2], not only to better approximate the efficiency of the composite in real conditions, which tend to be at such low concentrations, but also to perceive the effect of heavy metal concentration on the removal efficiency of the composite.

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