Using some Natural Minerals to Remove Cadmium from Polluted Water

Monier M. Wahba, Wafaa M. Hashesh, Nesreen H. Abou-Baker

Soils & Water Use Department, National Research Centre, Dokki, Giza, Egypt.
*Corresponding author: nh.abou-baker@nrc.sci.eg, nesreenhaa@yahoo.com
E-mails address: mm.wahba@nrc.sci.eg, wd.mohamed@nrc.sci.eg

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Abstract:
Water scarcity is one of the most important problems facing humanity in various fields such as economics, industry, agriculture, and tourism. This may push people to use low-quality water like industrial-wastewater. The application of some chemical compounds to get rid of heavy metals such as cadmium is an environmentally harmful approach. It is well-known that heavy metals as cadmium may induce harmful problems when present in water and invade to soil, plants and food chain of a human being. In this case, man will be forced to use the low quality water in irrigation. Application of natural materials instead of chemicals to remove cadmium from polluted water is an environmental friendly approach. Attention was drawn in this research work to use some natural minerals as zeolite, bentonite and montmorillonite to adsorb cadmium element from polluted water. Various concentrations of cadmium in solutions 10, 30 and 50 ppm were treated with three different ratios of each mineral; 1, 3 and 5% (W/V). The obtained results proved that increasing the ratio of amendments to 5% increased Cd adsorption from solution particularly at 50ppm Cd. Zeolite obtained the highest ratio of adsorption (47.90 ppm), followed by montmorillonite (44.99 ppm) and the lowest was bentonite (38.97 ppm). Therefore, it can be recommended that addition of zeolite is the most favorable material to remove Cd element from polluted water.

Keywords: Bentonite, Cadmium, Montmorillonite, Polluted water, Zeolite.

Introduction:
Heavy metal pollution is a serious problem facing the human being and other organisms due to their lack of biodegradation and accumulation in living organisms. There are many sources of the heavy metals in the eco-system which come with the wastewater streams such as Electro-plating, smelting, paint pigments, batteries, mining and agricultural activities. Cadmium is a very harmful and can pollute drinking and irrigation water. Cadmium can penetrate human body through food and thus can cause anemia, high blood pressure, muscle spasms, osteoporosis, and cancer and ultimately lead to death. The wide occurrence of Cd contamination in environment mainly originates from a range of anthropogenic sources, including fertilizers industry, battery industry (Cd-Ni battery), paint industry, and mining processes.

For reducing the hazardous effects of cadmium from polluted water, Hashesh et al. suggested using natural materials (zeolite, bentonite, and montmorillonite) could be a favorable economical alternative solution to reduce the risk of heavy metals in polluted water. The natural minerals are suitable materials for removing heavy metals from industrial waste. In addition, Atkovska et al., showed that bentonite and zeolite are widely used as conventional absorbent materials to remove various heavy metals such as Cd from polluted solutions. The ability of natural minerals as inorganic sorbent to adsorb heavy metals comes from their exchangeable capabilities, the high surface area, and the negative charging on their metal structure. Zeolite has a three-dimensional silicate frame; its structure withstands negative charges which can be balanced by absorbing interchangeable cations. Due to the very high amount of the natural zeolite, its stable structure even in the acidic environment, and its strong absorption capacity, it is used in industrial wastewater treatment. Also, it can be used in reducing biotic and abiotic stresses on plants. In another study, zeolite holds great potential to be
used as a filling material in interactive subsurface barriers to interrupt groundwater columns and for fixed-base reactors designed to adsorb heavy metals from industrial wastewater. It might be utilized to remove radioactive isotopes from polluted wastewater in an environmentally benign manner. Some types of zeolite have a net negative charge that is balanced by extra exchangeable cations. Bentonite is a one of 2:1 clay mineral that belongs to the smectite clay group with a single sheet of octahedral sandwiched between papers tetrahedral. Isomorphous substitutions within the octahedral sheets produce a negative surface charge. High potency of sodium bentonite to remove Cd ions from solutions even at very small loading where removal of more than 85% for each of the mineral ions is achieved with an absorbent content of 0.5 g/L. With the adsorbent dose increased to 0.8 g/L, the removal percentage increased to 92%, which could be linked to the most active sites available for absorption when the adsorbent content increased. Actually, zeolite, bentonite, montmorillonite and their mixture were used for reducing the effect of heavy metals on plant growth.

This work aims at studying the parameters that affect cadmium removal rates, such as the application dose of some natural minerals, the concentration of initial solution and the differences among the most spared sorbent minerals (zeolite, bentonite, montmorillonite). In addition, the maximum capacity of the adsorption of these minerals, which used to remove the studied metal ions through equilibrium reactions, was determined.

### Materials and Methods:

Batch experiments technique used to investigate sorption characteristics of cadmium onto three natural minerals (montmorillonite, bentonite and zeolite) at rates 1, 3 and 5% (W/V) from different concentrations of Cd polluted aqueous solutions (10, 30 and 50 mg L⁻¹). In three replicates, these minerals were weighed into 50 ml centrifuge tubes containing 25 ml of prepared solutions of Cd⁺² (10, 30 and 50 mg L⁻¹). The suspensions were shaken mechanically for 24 hrs. After equilibrium, the suspension was centrifuged at 3000-5000 rpm for 10-20 min. Equilibrium concentration of heavy metal (Ce) was determined in 1 ml of supernatant using Atomic Absorption Spectroscopy (AAS). There were differences between Ci “initial concentration of Cd” and Ce assumed to adsorb on adsorption materials. The concentration of HMs adsorbed on the minerals, Cs (mmol L⁻¹) expressed by equation: 

\[ Cs = Cl - Ce. \]

Sorption isotherms curves were obtained by plotting (Cs = conc. of HMs adsorbed on the sorbent mineral in mg kg⁻¹) versus Ce = mg per liter). The stock solutions of metal ions, having concentrations of 1000 mg L⁻¹ were prepared from cadmium nitrate Cd(NO₃)₂ in 1 mM HNO₃ acid. Cadmium concentration determined by atomic absorption (Perkin Elmer-AAnalyst 400) as described by. The three types of natural sorbent minerals namely bentonite, montmorillonite and zeolite (clinoptilolite) from ALIX Company were used in batch experiments. Some of physico-chemical properties of these materials are presented in Tables (1, 2 and 3).

### Results and Discussion:

With respect for the influence of the natural minerals type on cadmium, retention data of (Table 4) indicate that zeolite is more efficient to adsorb high amount of Cd followed by montmorillonite and bentonite, respectively. The mean values of adsorbed cadmium by zeolite average over all concentrations were 19.52, 23.92 and 28.31 ppm with increasing the rate of zeolite from 1, 3 and 5%, respectively. The structure of zeolite helps to adsorb relatively high quantity of cadmium. Abadeh and Irannajad investigated that the structure of zeolites
has a framework silicate with a three-dimensional cage structure. Its structure bears negative costs, which can be balanced by absorbing interchangeable cations. Due to the high natural zeolite deposits, its stable structure, and its strong adsorption capacity, it is used in industrial processing wastewater. It is clearly shown that the highest amount of adsorbed Cd was 47.91 ppm with 5% of zeolite and 50 ppm Cd while the least amount of adsorption was 5.12 ppm with 1% zeolite at 10 ppm Cd.

The Data in (Table 4) reveal that the values of adsorbed cadmium by 1% zeolite increased with increasing Cd concentration from 10 to 50 by about 51.20 and 71.38%, respectively. Zeolite is a very porous alumino-silicate with three-dimensional contiguous frameworks connected, it contains pores capable of taking molecules up to one nanometer in size and pore engineering can include cages and/or channels. Generally, zeolite ability to exchange cations and remove heavy metals from industrial wastewater is one of its most beneficial properties; this may be attributed to its structure described in terms of size, geometry and connection of the pore space. Dstan and Dehghani showed the effectiveness of natural zeolite in removing cadmium from industrial waste with 98% efficiency. However, increasing the dose of applied minerals resulted in a decrease in the percentage of retained Cd (Fig. 1). These percentages when Cd concentrations increased from 10 to 50 ppm were 91.50 and 95.82% at rate of 5%, respectively. Sanchez and Pariente showed that zeolite has a silicate frame for a 3-dimensional cage structure. Its structure withstands negative charges, which absorb interchangeable cations to be balanced. In addition, zeolite structure is distinguished in terms of pores size, their geometry, and connectivity. The ability to exchange cations is a useful characteristic and determines their ability to remove HMs from wastewater.

These results are in agreement with those obtained by Abd El-Azim and Fekry where they confirmed that zeolite has a great potential to remove HMs from industrial wastewater by adsorption.

In the case of montmorillonite, the mean values of adsorbed cadmium by montmorillonite were 35.00, 52.06 and 58.22 % with increasing the concentration of Cd from 10, 30 and 50 ppm at rate of 1% montmorillonite, respectively. The values in (Table 4) which illustrated in (Fig.2) indicate that the highest amount of adsorbed Cd was 45 ppm with the addition of 5% montmorillonite to the highest polluted solution (50 ppm Cd) while the least amount of adsorption was 5.12 ppm with addition of 1% montmorillonite to the lowest polluted solution (10 ppm Cd). These results are in agreement with those reported by Talaat et al. who pointed out that montmorillonite good absorbance.
to remove toxic heavy metals as (Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn). This may be attributed to two different mechanisms: I) cation exchange in the interlayer resulting from the interactions between ions and negative permanent charge, II) formation of inner-sphere complexes through Si–O- and Al–O_groups at the clay particle edges.

Data in Table (4) reveal that the values of adsorbed cadmium by montmorillonite increased with increasing Cd concentration from 10 to 50 by 82.10% and 89.98% at a dose of 5% montmorillonite, respectively. For applying bentonite mineral with cadmium, Table (4) shows that the mean values of retained cadmium by bentonite were 11.61, 18.25 and 22.84 ppm with increasing the dose of bentonite from 1, 3 to 5%, respectively. These results agree with Atkovska et al. who concluded that the substance of bentonite is used widely as a traditional absorbent to remove Cd^{2+} from wastewater. Also the values of retained cadmium by bentonite increased with increasing the Cd concentration from 10 to 50ppm by about 2.87 and 21.50 ppm at rate of 1% of bentonite, respectively.

Figure 3 illustrates the amount of retained cadmium at different rates of bentonite with different cadmium concentrations. The highest amount of retained cadmium was 38.97ppm at 5% applied bentonite and 50ppm of cadmium while the lowest adsorbed amount was 2.87ppm at 1% bentonite and concentration of 10-ppm cadmium. Ranga showed that bentonite is an excellent adsorbent of toxic metals from wastewater, which has been more on ways to focus adjustment, and thus increased its ability to absorb heavy metals. In this point, Ghomri et al. suggested that natural bentonite is a suitable absorbent material to absorb metal ions from aqueous solutions. Atkovska et al. reported that the substance of bentonite and zeolite is used widely as a conventional absorbent in removing Cd^{2+} from wastewater.

On the other hand, (Fig 4) illustrates the quantity of retained cadmium from water as affected by three rates of zeolite, montmorillonite and bentonite (1, 3 and 5% W/V). Wherever, increasing the dose of the natural sorbent minerals increased the amount of retained cadmium. It appeared clearly that bentonite exhibits the lowest values of cadmium retention as compared with the other minerals.

Conclusion:
Using some natural minerals as sorbent materials in mitigating the hazardous effect of cadmium is better than using chemical treatment as
it doesn't leave harmful effects in the soil. The superiority of zeolite in removing cadmium compared with montmorillonite and bentonite is attributed to its composition, crystal structure, and the ionic diameter of Cd. The results also showed that the high dose of amendments gave the greater quantity of removed cadmium. Therefore, it is preferable to use natural materials like zeolite, montmorillonite, and bentonite than chemicals in water treatment. Further studies on the effect of pH, time, temperature and the initial concentration of pollutants are required on the adsorption efficiency of different minerals and organo-mineral composites.

Authors’ declaration:
- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for re-publication attached with the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee in National Research Centre, Egypt.

Authors' contributions statement:
All authors conceived of the presented idea. A. M. verified the analytical methods. N. H. performed the computations and contributed in writing. M. M. supervised the findings of this work and discussed the results.

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استخدام بعض المعادن الطبيعية لإزالة الكادميوم من المياه الملوثة

منير مراد وهبه
نسرین حسین ابو بكر
قسم الأراضي و استغلال المياه، المركز القومي للبحوث، مصر.

الخلاصة:

تعد مشكلة ندرة المياه من أهم المشاكل المتواجدة الإنسان في مختلف المجالات المعيشية والاقتصادية مثل مجال الصناعة والزراعة، وقد أدت هذه اللقاحات إلى استخدام المواد الكيميائية في التخلص من العناصر الثقيلة مثل الكادميوم، لكنها ضرورية للبيئة من حيث الناحية البيئية. وبالتالي فإن استخدام المواد الطبيعية بدلاً من المواد الكيميائية هي الأفضل في هذا البحث. تم استخدام بعض المعادن الطبيعية مثل المونتموريلنيت، البنتونيت، والزئوليت لمسح الكادميوم من المياه. وتمت معالجات الهبس في المحاليل 10، 30، و 50 جزء في المليون وتم معالجتها بلزن نسبة مختلفة لكل معين (1 و 3 و 5٪ وزن إلى حجم). وقد أثبتت النتائج التي تم الحصول عليها أن زيادة نسبة المضافة إلى 5٪ تزيد من إمتصاص الكادميوم من المحلول خاصة عند تركيز 50 جزء في المليون من الكادميوم. حصل الزئوليت على أعلى نسبة إمتصاص (47.90 جزء في المليون) ، وليه مونتموريلنيت (44.99 جزء في المليون) وأقل نسبة كانت للبنتونيت (38.97 جزء في المليون). لذلك يمكن التوصية بأن إضافة الزئوليت هي الماده الأكثر ملاءمة لإزالة عنصر Cd من المياه الملوثة.

الكلمات المفتاحية: بنتونيت، كادميوم، مونتموريلنيت، مياه ملوثة، زئوليت.