Open Access **Baghdad Science Journal** **P-ISSN: 2078-8665**
Published Online First: March 2022 **2022, 19(5): 1008-1013** **E-ISSN: 2411-7986**

DOI: http://dx.doi.org/10.21123/bsj.2022.5385

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

Received 30/6/2020, Accepted 28/12/2021, Published Online First 20/3/2022, Published 1/10/2022

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[1].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[2]. Cadmium is a very harmful and can pollute drinking and irrigation water [3]. 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[4].The wide occurrence of Cd^{2+}contamination in environment mainly originates from a range of anthropogenic sources, including fertilizers industry, battery industry (Cd-Ni battery), paint industry, and mining processes [5].

For reducing the hazardous effects of cadmium from polluted water, Hashesh et al. [6] 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., [7] showed that bentonite and zeolite are widely used as conventional absorbent materials to remove various heavy metals such as Cd^{2+} 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[8]. Zeolite has a three-dimensional silicate frame; its structure withstands negative charges which can be balanced by absorbing interchangeable cations[9]. 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[10,11]. 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[12]. It might be utilized to remove radioactive isotopes from polluted wastewater in an environmentally benign manner[13]. Some types of zeolite have a net negative charge that is balanced by extra exchangeable cations[14]. 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[15]. Isomorphic substitutions within the octahedral sheets produce a negative surface charge[16]. High potency of sodium bentonite to remove Cd^{2+} ion 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[17]. Actually, zeolite, bentonite, montmorillonite and their mixture were used for reducing the effect of heavy metals on plant growth[18].

This work aims at studying of 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 50mg 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 50mg L^{-1}). The suspensions were shaken mechanically for 24 hrs. After equilibration, 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 ($mmolL^{-1}$) expressed by equation: Cs = Ci - 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 $Cd(NO_3)_2$ in1 mM HNO_3acid. Cadmium concentration determined by atomic absorption (Perkin Elmer-AAnalyst 400) as described by[19]. 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).

Table 1. The chemical composition and properties of used zeolite in the study

CEC Cmole Kg^{-1}	Surface area ($m^2 g^{-1}$)	pH 1:2.5	K_2O	Na_2O	Elements oxides (%)			
					SiO_2	Al_2O_3	Fe_2O_3	CaO
220	89.82	6.8	3.27	0.78	62.220	11.096	4.033	3.583

Table 2. Particle size distribution and some chemical properties of bentonite

Particle size distribution (%)					pH 1:2.5	EC dS/m	$CaCO_3$ g Kg^{-1}	CEC cmolc Kg^{-1}
C.sand	F.sand	Silt	Clay	Text. class				
1.1	3.8	5.3	89.8	Clay	8.3	4.10	27.3	53.2

Table 3. The chemical composition and properties of montmorillonite used in the study

Color	Purity (%)	pH 1:2.5	Maximum moisture (%)	CEC cmolcKg^{-1}	Chemical structure
Off white	> 98	6.8	89.82	116	Natural montmorillonite MMT M+y (Al_2-y Mgy) (Si_4) $O_{10}(OH)_2nH_2O$

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 28.31ppm 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[9] investigated that the structure of zeolites has a framework silicate with a three-dimension al 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 47.91ppm 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.

Table 4.The percentage of removal cadmium (%) by zeolite, montmorillonite and bentonite.

Natural minerals	Rate	Cd(10)	Cd(30)	Cd(50)	Mean
Zeolite	1%	51.20	59.17	71.38	60.58
	3%	71.40	79.37	81.64	77.47
	5%	91.50	92.93	95.82	93.42
Mean		41.40	78.27	82.94	
	1%	35.00	52.07	58.22	48.43
Montmorillonite	3%	59.80	69.90	79.96	69.89
	5%	82.10	86.60	89.98	86.23
Mean		59.00	67.30	76.06	
	1%	28.70	34.90	43.00	35.53
Bentonite	3%	49.80	56.23	65.78	57.27
	5%	72.30	74.43	77.94	74.89
Mean		50.30	53.60	62.24	

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[10, 20]. 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[9]. Dstan and Dehghani[21] 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[22] 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[22].

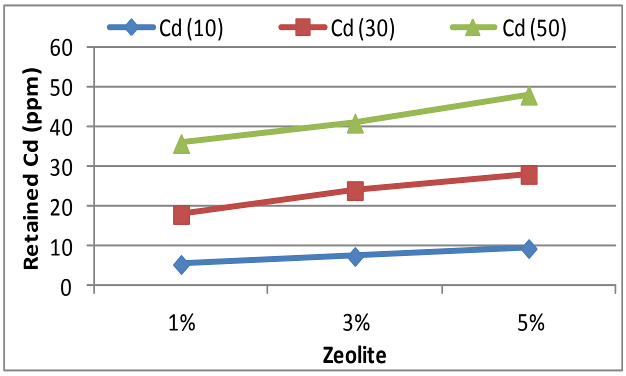

Figure 1. Cadmium removal from aqueous solutions by different rates zeolite.

These results are in agreement with those obtained by Abd El-Azim and Fekry[15] 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 3.50 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.[23] 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[24].

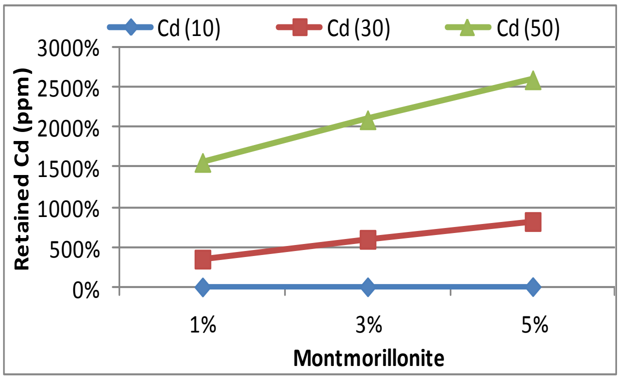

Figure 2. Cadmium removal from aqueous solutions by different rates of montmorillonite.

Data in Table (4) reveal that the values of adsorbed cadmium by montmorillonite increased with increasing Cd concentration from10 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.[7] 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 from10 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% of applied bentonite and 50ppm of cadmium while the lowest adsorbed amount was 2.87ppm at 1% bentonite and concentration of 10-ppm cadmium. Ranga[25] 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.[26] suggested that natural bentonite is a suitable absorbent material to absorb metal ions from aqueous solutions. Atkovska et al.[7] reported that the substance of bentonite and zeolite is used widely as a conventional absorbent in removing Cd^{2+} from wastewater.

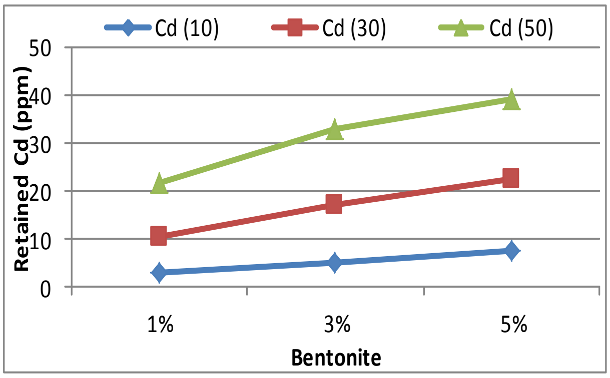

Figure 3. Cadmium removal from aqueous solutions by different rates of bentonite.

Figure 4 shows the comparison between quantities of retained cadmium from polluted liquid also affected zeolite, bentonite and montmorillonite application. Zeolite minerals obviously retained higher amount than bentonite and montmorillonite respectively. The highest percent of retained cadmium was 47.91ppm at 5% zeolite followed by montmorillonite and bentonite that gave values of 44.99, 38.97ppm, respectively. Mohsen et al.[27] suggested that zeolite is more effective for the treatment of wastewater.

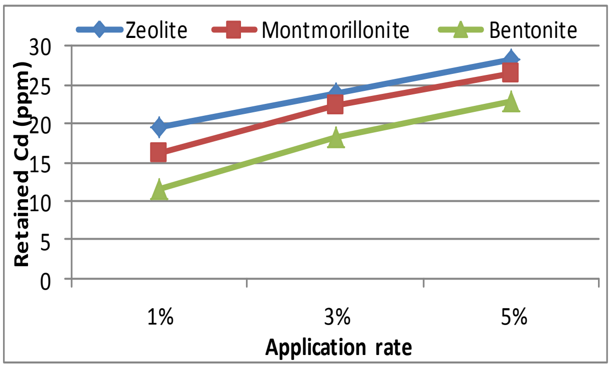

Figure 4. Retained cadmium from aqueous solutions using different rate of zeolite, montmorillonite and bentonite.

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 and5% 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. W. 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.

References:

1. Maleki A, Mahvi AH, Zazouli MA, Izanloo H, Barati AH. Aqueous cadmium removal by adsorption on barley hull and barley hull ash. Chem. Asian J. 2011; 23(3): 1373-1376.
2. Ibrahim WM, Mutawie HH. Bioremoval of heavy metals from industrial effluent by fixed-bed column of red macroalgae. ToxicolInd Health. 2013; 29(1): 38-42.
3. Mata Y, Blázquez M, Ballester A, González F, Munoz J. Biosorption of cadmium, lead and copper with calcium alginate xerogels and immobilized Fucusvesiculosus.J. Hazard. Mater. 2009; 163(2-3): 555-562.
4. Tanzifi M, KolbadiNezhad M, Karimipour K. Kinetic and isotherm studies of cadmium adsorption on polypyrrole/titanium dioxide nanocomposite. J Water Environ Nanotechnol. 2017; 2(4): 265-277.
5. Barsbay M, KavaklPA, Tilki S, Kavaklı C, Güven O. Porous cellulosic adsorbent for the removal of Cd (II), Pb (II) and Cu (II) ions from aqueous media. Radiat. Phys. Chem. 2018; 142: 70-6.
6. Hashesh WM, Habib F, Wahba M, Noufal EH, Abou-Baker NH. Removal of lead from polluted water by using clay minerals. Zagazig J Agric Res. 2017; 44(6): 2097-2103.
7. Atkovska K, Lisichkov K, Ruseska G, DimitrovAT, Grozdanov A. Removal of heavy metal ions from wastewater using conventional and nanosorbents: a review. J ChemTechnol Metall. 2018; 53(2): 202-219.
8. Taamneh Y, Sharadqah S. The removal of heavy metals from aqueous solution using natural Jordanian zeolite. Appl water sci. 2017; 7(4): 2021-2028.
9. Abadeh ZA, Irannajad M. Removal of Ni and Cd ions from aqueous solution using iron dust-zeolite composite: Analysis by thermodynamic, kinetic and isotherm studies. Chem Res Chin Univ . 2017; 33(2): 318-326.
10. Abou-Baker NH, Ibrahim EA, Abd-Eladl MM. Biozeolite for improving bean production under abiotic stress conditions. Bull. Transilv. Univ. Bras. II: For. Wood Ind. Agric. Food Eng.. 2017;10(59):151-170.
11. Abd El-Zaher FH, Lashein A, Abou-Baker NH. Application of zeolite as a rhizobial carrier under saline conditions. Biosci Res. 2018;15(2):1319-33.
12. Khachatryan SV. Heavy metal adsorption by armenian natural zeolite from natural aqueous solutions. Chem. Biol. 2014; 2: 31-35.
13. Tuaimah SK, Al-Nasri SK, Al-Rahmani AA. Using Dates Leaves Midribs to Prepare Hierarchical Structures Incorporating Porous Carbon and Zeolite A Composites for Cesium137Cs Ion Exchange. Baghdad sci J. 2020 Jul 16; 17(3): 818-825.
14. Ugal JR, Kareem SH, Hassan SS. Adsorption of hydrogen sulphide on the zeolite type Asynthezied from Iraqi kaoline. Baghdad SciJ . 2013; 10: 1023-1033.
15. Abd El-Azim H, Mourad FA. Removal of Heavy Metals Cd (II), Fe (III) and Ni (II), from aqueous solutions by natural (clinoptilolite) zeolites and application to industrial wastewater. Asian J Environ Sci. 2018:1-13.
16. Guerra D, Mello I, Resende R, Silva R. Application as absorbents of natural and functionalized Brazilian bentonite in Pb^{2+} adsorption: Equilibrium, kinetic, pH, and thermodynamic effects. Water Resour Ind. 2013; 4: 32-50.
17. Burham N, Sayed M. Adsorption behavior of Cd^{2+} and Zn^{2+} onto natural Egyptian bentonitic clay. Minerals. 2016; 6(4): 129.
18. Abou-Baker NH, El-Ashry MS, Wahba MM, Habib FM, Noufal EHA, Hashesh WM. Evaluating the Application of some Natural Amendments to Hinder the Pollution of Barley Plants by Heavy Metals. Sci J King Faisal Univ. 2019, 20 (2-1441H): 55-68.
19. Cottenie A, Verloo M, Kiekens L, Velghe G, Camerlynch R. Chemical analysis of plants and soils. Laboratory of Analytical and Agrochemistry State University, Ghent Belgium. 1982. Article No. 42, 80-284
20. Bu X, Feng P, Stucky GD. Large-cage zeolite structures with multidimensional 12-ring channels. Science. 1997; 278(5346): 2080-2085.
21. Dstan L, Dehghani M. Removal of cadmium from industrial waste water by adsorption zeolite

clinoptilolite. BiosciBiotechnolRes Commun. 2016;9(4):865-871.
22. Pariente PJ, Sanchez MC. Zeolites and ordered porous solids: fundamentals and applications: Editorial UniversitatPolitècnica de València; 2011. http://hdl.handle.net/10251/11205
23. Talaat H, El Defrawy N, Abulnour A, Hani H, Tawfik A. Evaluation of heavy metals removal using some Egyptian clays.2nd International Conference on Environmental Science and Technology. IACSIT Press, Singapore. IPCBEE. 2011; 6: 37-42.
24. Kraepiel AML, Kellers K, Morel FMM. A model for metal adsorption on montmorillonite. J Colloid Interface Sci.1999; 210(1):43-54.
25. Ranga S. Bentonite used as natural coagulant and adsorbent: A review. J Pharm Innov. 2018; 7(7): 155-157.
26. Ghomri F, Lahsini A, Laajeb A, Addaou A. The removal of heavy metal ions (copper, zinc, nickel and cobalt) by natural bentonite. Larhyss j.2013(12). P-ISSN 1112-3680/E-ISSN 2521-9782..
27. Hamidpour M, Kalbasi M, Afyuni M, Shariatmadari H, Holm PE, Hansen HC. Sorption hysteresis of Cd(II) and Pb(II) on natural zeolite and bentonite. J Hazard Mater. 2010; 181: 686–691.

استخدام بعض المعادن الطبيعية لإزالة الكادميوم من المياه الملوثة

منير مراد وهبه **وفاء محمد حشيش** **نسرين حسين ابو بكر**

قسم الاراضى و استغلال المياه، المركز القومى للبحوث، مصر.

الخلاصة:

تعد مشكلة ندرة المياه من اهم المشاكل التىتواجه الانسان فى مختلف المجالات المعيشية والاقتصادية مثل مجال الصناعة والزراعة و السياحة مما يدفع الانسان لاستخدام المياه منخفضة الجوده كمياه الصرف الصناعى. ويعتبر استخدام بعض المركبات الكيميائية فى التخلص من العناصر الثقيلة مثل الكادميوم هو نهج ضار بالبيئة. و من المعروف جيدًا أن عنصر الكادميوم يسبب مشاكل كبيرة عند وجوده في الماء ومن ثم يغزو التربة والنباتات والسلسلة الغذائية للإنسان. وبالتالى فان استخدام المواد الطبيعية بدلاً من المواد الكيميائية لإزالة الكادميوم من المياه الملوثة نهجصديقًا للبيئة. لذلك تم التركيز في هذا البحث على استخدام بعض المعادن الطبيعية مثلالمونتموريلونيتوالبنتونيتوالزيوليتلامتصاص عنصر الكادميوم من المياه الملوثة. و قد استخدمت تركيزات مختلفة من الكادميوم في المحاليل 10 و 30 و 50 جزء في المليون و تم معالجتها بثلاث نسب مختلفة لكل معدن (1 و 3 و 5٪ وزن الى حجم). وقد أثبتت النتائج التي تم الحصول عليها أن زيادة نسبة الاضافات إلى 5٪ تزيد من امتزاز الكادميوم من المحلول خاصة عند تركيز 50 جزء في المليون من الكادميوم. حصل الزيوليت على أعلى نسبة امتزاز (47.90 جزء في المليون) ، يليه مونتموريلونيت (44.99 جزء في المليون) وأقل نسبة كانت للبينتونيت (38.97 جزء في المليون). لذلك ، يمكن التوصية بأن إضافة الزيوليت هي المادة الأكثر ملاءمة لإزالة عنصر Cd من المياه الملوثة.

الكلمات المفتاحية: بنتونيت ،كادميوم ، مونتموريلونيت ، مياه ملوثة ، زيوليت .