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Adsorption of some heavy metals and (Mg^{+2}, Ca^{+2}) ions from aqueous solutions by using different environmental residuals as a cheap adsorbents at optimum conditions

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Abstract: In this study, removal of some heavy metals ions (Hg^{2+}, Pb^{2+}, and Zn^{2+}) from aqueous solution and (Mg^{+2} ,Ca^{+2}) ions by adsorption process was investigated. The commercial activated carbon (Merck 2514), silica and ceramic were used as adsorbents. The adsorption process was carried out at the pH range from 5.3 to 5.5 and at room temperature. In this work 100% adsorption uptake was obtained in some cases. Amounts of metal adsorbed q_e was calculated and the uptake percent was also calculated.

Keywords: Heavy Metals , Activated Carbon, Adsorption , Ceramic, Environmental residuals

1. Introduction

The problems of the ecosystem are increasing with developing technology. Heavy metal pollution is one of the main problems. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's waters may contain various toxic metals. Drinking water is obtained from springs which may be contaminated by various toxic metals. One of the most important problems is the accumulation of toxic metals in food structures. As a result of accumulation, the concentrations of metals can be more than those in water and air. The contaminated food can cause poisoning in humans and animals. Although some heavy metals are necessary for the growth of plants, after certain concentrations heavy metals become poisonous for both plants and heavy metal microorganisms. Another important risk concerning contamination is the accumulation of these substances in the soil in the long term. It has been determined that various metal ions hinder various enzymes responsible for mineralization of organic compounds in the earth [1-4]. Therefore, studies on the removal of heavy metal pollution are increasing. The purpose of this study was to investigate the removal of some toxic heavy metals from aqueous solution by adsorption, to determine the optimum removal condition by using different types of adsorbents. Activated carbon is widely used as an adsorbent in industry due to its high adsorption capacity. This capacity is related to the pore structure and chemical nature of the carbon surface in connection with preparation conditions [5]. The "Ceramic Membrane Filtration System" is a reliable technology to produce clean water by removing the turbidity, bacteria, and cryptosporidium and other protozoa contained in raw water sources such as surface water and ground water [6-8]. Using a unique ceramic membrane as a filter, this system is a low cost and long life filtration system. Therefore it can enable a water supply system to meet recent demands for safe and tasty water. In recent years; there is an increase interest in using non-chemical and low-cost adsorbent to remove heavy metals from wastewater. Mesoporous silica materials[9,10] have attracted attention because of their utilities in adsorption, selective separation and catalysis [11,12] MCM-41, one of the important mesoporous materials, has excellent periodicities in the mesoporous channels, larger BET surface area, high porosities and narrow pore sizes[13-15]. Initial studies of the self-assembled silica having a two-dimensional hexagonal ordering of cylindrical mesopores stimulated activities on the preparation of several mesoporous materials using alkyl trimethyl ammonium surfactants of varying alkyl chain length as structure directing agents. Metal ion adsorbents have been prepared by grafting thiol functional groups as a monolayer onto the inner surface of MCM-41[16,17]. Thiol functionalized MCM-41 was proved to be efficient adsorbents for mercury and heavy metal ions. A few other reports are available on synthesis thiol and amine functionalized mesoporous materials and use of the functionalized MCM-41 as adsorbents for removal of heavy metal ions [18-21]. In the present work the other try find the best removal for heavy metals and Ca^{++} and Mg^{++} by low cost and high percent of adsorbent

2. Experimental

All Chemicals Analytical grad: EDTA, ZnSO4, $Mg(NO_3)_2$, $Ca(NO_3)_2$ $Hg(NO_3)2$, $Pb(NO_3)_2$, NH_4Cl, NH_4OH, Murexide, and EBT.

Adsorbents: activated carbon, ceramic powder and silica.

In this study, the adsorption of Zn^{2+}, Mg^{2+}, Ca^{2+}, Pb^{2+} and Hg^{2+} on commercial activated carbon, silica, and ceramic were investigated. One gram of adsorbents with 5 ml of initial concentrations (C_0) of 0.01 Molar of heavy metals was shaken at 15 mints. Amounts of sample were taken from solutions containing adsorbent. The solution was diluted and titration with EDTA Solution. The equilibrium concentrations of heavy metals were determined after taking amount of samples from clear parts of solutions containing adsorbent and doing proper dilutions. The amount adsorbed (C_0) was calculated from the difference between initial and equilibrium concentrations. Which adsorbent does more adsorption at 24 hours was determined without looking at the equilibrium contact times. For this, 1g of adsorbents with 5 ml of initial concentrations of0.01 Molar of these ions for determination of the percent of removal by adsorbents of heavy metals were shaken separately for 15 mints at 30C°. At the end of this period, the residual concentrations of heavy metals which were not adsorbed were determined with titration of EDTA.

1 Preparation of 0.01 M of ions solutions .
2 In this study, the adsorption of Mg^{2+}, Ca^{2+}, Hg^{2+} ,Pb^{2+} and Zn^{+2} on 2514 commercial activated carbon , ceramic and silica were investigated. One gram of each absorbent with 5 ml of initial concentrations of ions and string them 15 mint.
3 Preparation of 0.01 M of EDTA solution.
4 Standardization of EDTA by ZnSO4.
5 Determination initial concentration of different ions by use EDTA before treatment.
6 Determination finial concentration of different ions by use EDTA after treatment.
7 Titration each solution of ions before and after treatment by EDTA.
8 The percentage removal of elements and the amount of element adsorbed on adsorbent (qe) were:

Calculated, respectively, as follows [9]:

$$\%Removal = (C_0\text{-}Ce/C_0)\ x100$$

$$qe = (C_0\text{-}Ce/M)V$$

where qe is the amount of ion adsorbed on adsorbent at equilibrium, C_0 and Ce are the initial and equilibrium of element concentration in solution, respectively, V is the volume of solution (L), and M is the weight of adsorbent (g).

3. Results and Discussion

Effect of different adsorbents: This effect was studied using of activated carbon, ceramic and silica (dose 1 g) at room temperature was shown in tables. The results show that the percentage of adsorption was increased when used a mixed of adsorbents. It is apparent that by increasing the number of sorption sites available for sorbent-bio - solute interaction is increased, there by resulting in the increased percentage of elements removal from the solution. But when used one adsorbent be that the percentage of adsorption was decreased and observed that there are high percentage of adsorption for some elements by one adsorbent like Hg^{+2} with activated carbon show table 1, pb^{+2} with ceramic show table 2 and Mg^{+2} with silica show table 3. When used three layers of adsorbents the percentage of adsorption was increased and obtained 100% removal for all elements ions show table 7. Table 8 displays that the best absorbent for Pb^{+2} is Ceramic, the best absorbent for Hg^{+2} is activated carbon , the best absorbent for Zn^{+2} and Ca^{+2} is silica [26] and the best absorbent for Mg^{+2} is silica and activated carbon. Table 9 displays that the best absorbent for Pb^{+2} and Hg^{+2} is activated carbon with silica and ceramic with activated carbon[27], the best absorbent for Zn^{+2} and Mg^{+2} is silica with ceramic and activated carbon ceramic the best absorbent for Ca^{+2} is silica with activated carbon. Table 10 displays that the best filter for removal heavy metals is contain three layers of activated carbon with silica and ceramic[28] where obtain 100% of absorbance for ions.

Table (1). *Effect of Activated carbon on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe).*

Element	Pb^{+2}	Hg^{+2}	Zn^{+2}	Ca^{+2}	Mg^{+2}
%Removal	70%	100%	80%	90%	90%
qe	0.035	0.05	0.04	0.045	0.045

Table (2). *Effect of ceramic on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe).*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	100%	20%	64%	20%	80%
qe	0.05	0.01	0.032	0.01	0.04

Table (3). *Effect of silica on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe).*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	90%	98%	90%	90%	98%
qe	0.045	0.049	0.045	0.045	0.049

Table (4). *Effect of Activated carbon with ceramic on The percentage removal of elements and the amount of element adsorbed on adsorbent (qe).*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	100%	100%	100%	56%	100%
qe	0.025	0.025	0.025	0.014	0.025

Table (5). *Effect of Activated carbon with silica on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe).*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	100%	100%	96%	98%	98%
qe	0.025	0.025	0.024	0.0245	0.0245

Table (6). *Effect of ceramic with silica on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe)*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	0.94%	80%	100%	80%	100%
qe	0.0235	0.02	0.025	0.02	0.025

Table (7). *Effect of Activated carbon with silica and ceramic on the percentage removal of elements and the amount of element adsorbed on adsorbent (qe)*

Element	**Pb^{+2}**	**Hg^{+2}**	**Zn^{+2}**	**Ca^{+2}**	**Mg^{+2}**
%Removal	100%	100%	100%	100%	100%
qe	0.025	0.025	0.025	0.025	0.025

Table (8). *Effect of different adsorbents on removal of heavy metals, $Ca^{+2}$and Mg^{+2}.*

Elements	**Initial concentration] molar**	**Conc. after Treatment by silica**	**Conc. after treatment by ceramic**	**Conc. after treatment by activated carbon**
Pb^{+2}	0.01	0. 001	0	0.003
Hg^{+2}	0.01	0.0002	0.008	0
Zn^{+2}	0.01	0.001	0.0036	0.002
Ca^{+2}	0.01	0.001	0.008	0.001
Mg^{+2}	0.01	0.0002	0.002	0.001

Table (9). *Effect of different two mixtures of adsorbents on removal of heavy metals, $Ca^{+2}$and Mg^{+2}.*

Elements	**Initial concentration**	**Conc. after Treatment by activated carbon and ceramic**	**Conc. after treatment by ceramic and silica**	**Conc. after treatment by activated carbon and silica**
Pb^{+2}	0.01	0	0.0006	0
Hg^{+2}	0.01	0	0.002	0
Zn^{+2}	0.01	0	0	0.0004
Ca^{+2}	0.01	0.0044	0. 002	0.0002
Mg^{+2}	0.01	0	0	0.0002

Table (10). *Effect of different mixture of three adsorbents on removal of heavy metals, Ca^{+2} and Mg^{+2}*

Elements	Initial concentration	Conc. after Treatment by activated carbon , ceramic and silica
Pb^{+2}	0.01	0
Hg^{+2}	0.01	0
Zn^{+2}	0.01	0
Ca^{+2}	0.01	0
Mg^{+2}	0.01	0

Fig (1). *the filtrate before the treatment process*

Fig (2). *the filtrate after the treatment process*

The orders of adsorption of heavy metal ions for the activated carbon adsorbent change in the order of Pb^{2+} > Mg^{2+} > Zn^{2+} > $Ca^{2+}$and Hg^{+2} , in the order of Hg^{2+} > Ca^{2+} and Mg^{+2} > Zn^{2+} > pb^{2+} for ceramic and in the order of Hg^{+2} , Mg^{+2} > Zn^{2+}, Ca^{2+}, Pb^{2+} for silica show tables 1,2,3. It can be concluded that it is necessary for various adsorbents to be tested because of their different surface properties in the determination of optimum conditions in terms of adsorbents for removal of the heavy metals by adsorption from aqueous solution without changing the conditions. The reason for this is that a substance which is a good adsorbent for one adsorbate may not be a good adsorbent for another. we observed the removal percentage get 100% when we used the three adsorbents together .

4. Conclusion

It can be concluded that it is necessary for various adsorbents to be tested because of their different surface properties in the determination of optimum conditions in terms of adsorbents for removal of the heavy metals by adsorption from aqueous solution without changing the conditions. Various adsorbents have different adsorption capacities for a few of the toxic metal ions. The best absorbent for Hg^{+2} is activated carbon is apparent that by increasing the number of sorption sites, pb^{+2} with ceramic and Mg^{+2} with silica. When used three layers of adsorbents the percentage of adsorption was increased and obtained 100% removal for all elements ions decrease in textural parameters like pore diameter and pore volume are known to be the influencing factors for the adsorption efficiency. These adsorbents materials are suitable for adsorption of toxic metal ions.

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