Adsorption of Some Heavy Metal Ions from Aqueous Solution by Activated Carbon and Comparison of Percent Adsorption Results of Activated Carbon with those of Some Other Adsorbents

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In this study, removal of some heavy metals ions (Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}) from aqueous solution by adsorption was investigated. For this purpose, high-grade $MnSO_4.H_2O$, $FeSO_4.7H_2O$, $NiSO_4.7H_2O$ and $CuSO_4.5H_2O$ were used as heavy metal samples. The commercial activated carbon (Merck 2514), chitosan and agar were used as adsorbents. The pH of each solution was not controlled. This is because the net interaction between the adsorbent and the heavy metal could be disturbed by the buffer solution. Therefore, all experiments were carried out in a pH range from 5.3 to 5.5. The equilibrium adsorption contact times were determined for M - 2514. The adsorption rate constants were determined from obtained kinetics curves suitable for first degree of rate kinetics. Adsorption isotherms of heavy metals on M - 2514 from aqueous solution were determined. These adsorption isotherms were seen to be consistent with Freundlich's adsorption isotherm. k and n constants were determined from Freundlich's linear equation. In addition, M - 2514, chitosan and agar were compared according to their percent uptake yields of the heavy metals.

Key Words: Heavy metal adsorption, activated carbon, chitosan, agar, adsorption from aqueous solution, adsorption kinetics, adsorption isotherm.

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. Heavy metals are held in soil as a result of adsorption, chemical reaction and ion exchange of soil. Heavy metals have an effect on the enzymes. 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 adsorbents, to determine the suitable adsorption isotherms and to determine the related constants. 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 (5-7). In recent years, chitosan and agar have been commonly used to remove heavy metals and organic compounds from water and waste water (8-17). Chitosan is a polysaccharide derived from the deacetylation of chitin and forms the exoskeleton of crustacea and insects (12,17). Agar is a galactose polymer present in some sea plants of moss species. Galactose units in the agar structure are bound to each other with $1\beta O-4$ bonds (18).

Experimental

In this study, the adsorption kinetics of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} on M - 2514 commercial activated carbon were investigated. One gram of M - 2514 commercial activated carbon with 50 ml of initial concentrations (C_i) of 200 ppm of heavy metals was shaken at different time intervals at 140 rpm. Sufficient amounts of sample were taken from solutions containing adsorbent. The solution was diluted and analysed with a UNICAM 929 Atomic Absorption Spectrometer (AAS). Equilibrium adsorption times without any change of concentrations (C_r) remaining without adsorption of heavy metals were obtained from kinetic curves related to Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+}.

The adsorption isotherms of heavy metals were studied. For this purpose, 1g of M - 2514 commercial activated carbon with 50 ml of different initial concentrations of the heavy metals were shaken at their equilibrium contact times at 140 rpm at 30 °C. The equilibrium concentrations of heavy metals were determined after taking sufficient amount of samples from clear parts of solutions containing adsorbent and doing proper dilutions. The amount adsorbed (C_a) 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 50 ml of initial concentrations of 200 ppm of these for determination of the percent of removal by adsorbents such as M - 2514 commercial activated carbon, chitosan and agar of heavy metals were shaken separately for 24 hours at 140 rpm at 30 °C. At the end of this period, the residual concentrations of heavy metals which were not adsorbed were determined with the UNICAM 929 AAS. These procedures were applied after taking sufficient amounts from the clear parts of solutions containing adsorbent and doing proper dilutions.

Results and Discussion

Figure 1 displays the kinetic curves related to adsorption of Mn^{2+}, Fe^{2+}, N^{2+} and Cu^{2+} on M - 2514 commercial activated carbon. Equilibrium contact times from kinetic curves of heavy metals were determined to be 150, 140, 134 and 130 hours, respectively. These findings suggest that adsorption kinetic curves of

heavy metals fitted the kinetic curve of the first degree (Figure 2).

The greater adsorption rate constant shows that adsorbates are adsorbed faster by the adsorbent. According to adsorption rate constants, the heavy metal ions used are changing in the order of $Mn^{2+} <$ $Fe^{2+} < Ni^{2+} < Cu^{2+}$. This order was confirmed by equilibrium contact times determined from their kinetic curves.

Adsorption rate constants (k_a) were determined by using these curves (Table 1).
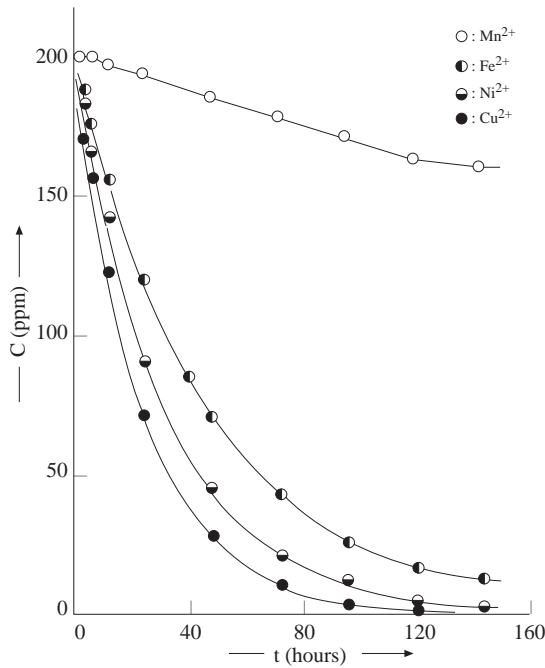

Figure 1. Kinetic curves related to adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution on M-2514
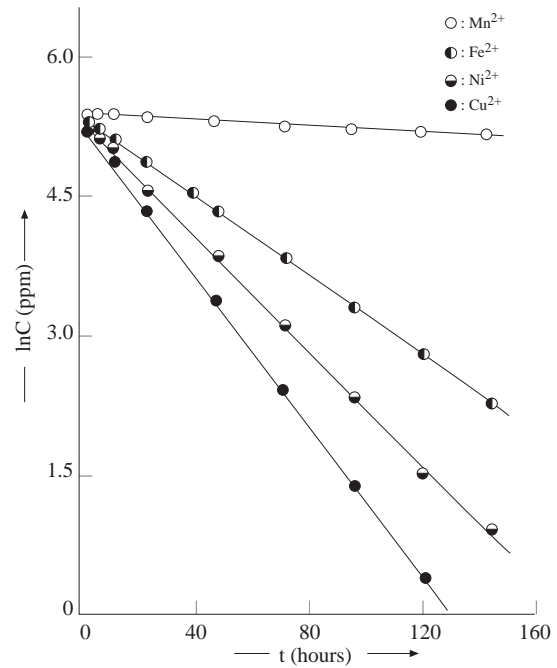
Figure 2. Kinetic curves of first degree related to adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution on M-2514.
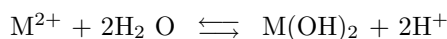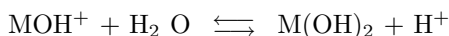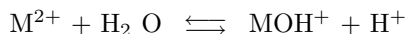
$$ln\frac{C}{C_i} = -k_a t \tag{1}$$

Table 1. Rate constants related to adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution by activated carbon

Adsorbate	k_a (h^{-1})
Mn^{2+}	0.0017
Fe^{2+}	0.0209
Ni^{2+}	0.0308
Cu^{2+}	0.0395

This result most probably arises from the differences between the hydrolysis constants and the ionic diameters of heavy metal ions. The hydrolysis reaction equilibrium mentioned below according to greatness of hydrolysis constants of heavy metal ions in Table 2, namely MOH^+ in the first step, is formed and the adsorption event is completed through prompt interaction of heavy metal ions with negative groups on activated carbon.

Table 2. Hydrolysis constants and ionic diameters of some heavy metals ions [19,20].

Heavy Metals Ions	Mn^{2+}	Fe^{2+}	Ni^{2+}	Cu^{2+}
pk_h	10.7	10.1	9.40	7.53
Ionic Diameters (pm)	80	76	72	70

$$M^{2+} + H_2O \; \longleftrightarrow \; MOH^+ + H^+$$

$$MOH^+ + H_2O \; \longleftrightarrow \; M(OH)_2 + H^+$$

$$M^{2+} + 2H_2O \; \longleftrightarrow \; M(OH)_2 + 2H^+$$

According to Pearson's hard acid-hard base theory, hard acid reacts to hard base. The hardness order of acidities of the heavy metal ions used is $Mn^{2+} > Fe^{2+} > Ni^{2+} > Cu^{2+}$. OH^- is also a hard base [19]. According to Pearson's theory and the greatness order above, Mn^{2+} reacts more with OH^-. Mn^{2+} is the most hydrolysed heavy metal ion of the ions above. The hydrolysed part of Mn^{2+} reacts with OH^- in a short time and $Mn(OH)_2$ is formed. Because there is no Mn^{2+} or much less Mn^{2+} in the medium, Mn^{2+} does not react or reacts a small amount with negative groups on the surface of the activated carbon. Accordingly, the amount of adsorbed Mn^{2+} is very small. It can be seen that heavy metal ions are being adsorbed when ionic diameters decrease. The ionic diameters of the heavy metals used change in the order of $Mn^{2+} > Fe^{2+} > Ni^{2+} > Cu^{2+}$ (Table 2). Since the activated carbon used is a microporous adsorbent [21], heavy metals penetrate easily into these pores when the ionic diameter becomes small [22]. According to the order above, Mn^{2+} must be the least adsorbed and Cu^{2+} must be the most adsorbed. This is compatible with our experimental results. The surface area of the activated carbon used in this study is 1160.3 m^2g^{-1}, its mesopore volume is 0.037cm^3g^{-1} and micropore volume is 0.384 cm^3g^{-1} [21].

The Irving-Williams series, that is, the order of complex stabilities of heavy metal ions used as absorbates is given as $Mn^{2+} < Fe^{2+} < Ni^{2+} < Cu^{2+}$ [19]. According to this order, Mn^{2+} must be the least adsorbed and Cu^{2+} must be the most adsorbed, because the heavy metal whose complex is stable will be present in the complex at higher levels and this will cause the complex to be adsorbed more. Our experimental results are consistent with this. Figure 3 displays the isotherms of adsorption related to Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution on M-2514 commercial activated carbon. It was seen that these isotherms fitted the Freundlich adsorption isotherm. Experimental data were also applied to the Langmuir adsorption isotherm, but the linear state of the Langmuir adsorption isotherm was not obtained. This consistency is seen in the Freundlich linear adsorption isotherm drawn according to equation 2[23] (Fig. 4). k and n constants peculiar to adsorbent and adsorbate were determined from the intercept and slopes of Freundlich linear adsorption isotherms (Table 3). The k-constant is concerned with the ability of the adsorbent to adsorb and the n-constant is concerned with

$$log_{10}C_a = log_{10}k + 1/n log_{10}C_e \tag{2}$$

tendency of the adsorbate to be adsorbed. As can be seen in Table 3, n constants of the heavy metal ions adsorbed change in the order of $Cu^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$. It is seen that the n constants obtained fit

the Irving-Williams series because the stable complex formed increases the ability of the heavy metal to be adsorbed and causes the n-constant to be high. This is compatible with our experimental results.

Table 4. includes the results of percent removal, calculated according to equation 3, of heavy metal ions used by activated carbon, chitosan and

$$R\% = \frac{C_i - C_r}{C_i}100 \tag{3}$$

agar. Greatness orders of adsorbents for removal of the heavy metals were determined as to be agar> activated carbon≥ chitosan for manganese, chitosan> activated carbon > agar for iron, chitosan > activated carbon > agar for nickel and chitosan > activated carbon > agar for copper (Table 4). It can be supposed that adsorbents adsorb the adsorbates in the order of the same greatness generally because of their selector properties. For example, as seen above, although Mn^{2+} is adsorbed less than the other heavy metals by both activated carbon
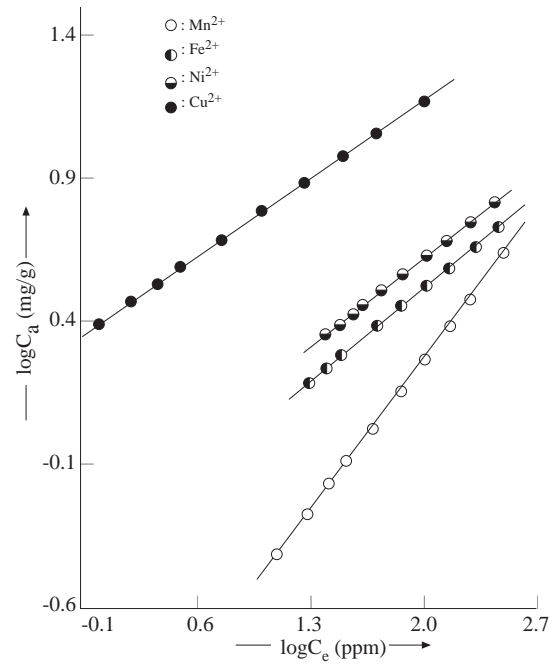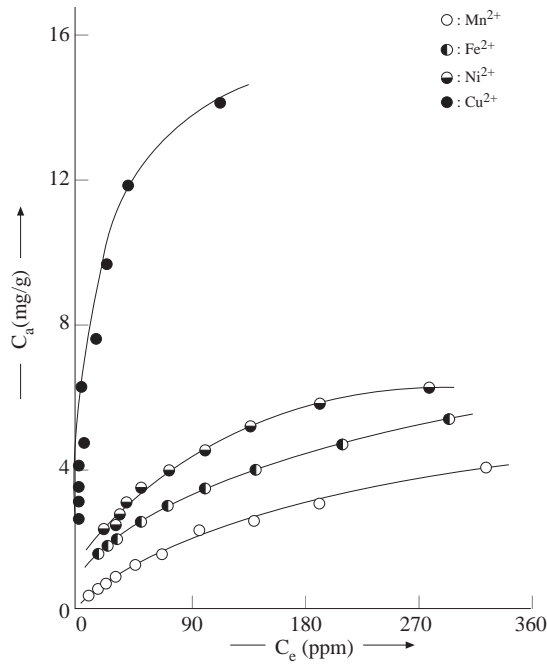

Figure 3. Adsorption isotherms related to Mn^{2+} , Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution on M- 2514.

Figure 4. Freundlich's linear isotherms related to adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution on M-2514.

Table 3. Freundlich's constants related to adsorption of Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution by activated carbon.

Adsorbate	k	n
Mn^{2+}	0.0574	1.3393
Fe^{2+}	0.3795	2.1751
Ni^{2+}	0.5256	2.2573
Cu^{2+}	2.3940	2.5786

Table 4. Percent removal (R %) results related to Mn^{2+}, Fe^{2+}, Ni^{2+} and Cu^{2+} from aqueous solution onto activated carbon, chitosan and agar.

Adsorbate	Adsorbent		
	Activated Carbon	Chitosan	Agar
Mn^{2+}	3.65	3.64	50.53
Fe^{2+}	40.30	80.60	39.48
Ni^{2+}	54.58	84.01	43.73
Cu^{2+}	63.99	99.25	48.71

and chitosan, it is adsorbed more as a selector than the other heavy metals by agar. The orders of adsorption of heavy metal ions for the same adsorbent change in the order of $Cu^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$ for activated carbon, in the order of $Cu^{2+} > Ni^{2+} > Fe^{2+} > Mn^{2+}$ for chitosan and in the order of $Mn^{2+} > Cu^{2+} > Ni^{2+} > Fe^{2+}$ for agar.

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.

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