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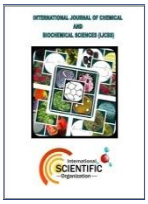

Removal of heavy metals (Zn, Cr, Pb, Cd, Cu and Fe) in aqueous media by calcium carbonate as an adsorbent

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Abstract

The adsorption of heavy metals ions in continuous flow column having calcium carbonate as adsorbent was carried at laboratory scale. The aqueous solutions of heavy metal passed through column having bed of precipitated $CaCO_3$. The concentration of each metal was determined by atomic absorption spectrometer before and after treatment. The significant decrease in the concentration of all metal ions was observed after treatment. The initial concentration of metals such as Zn^{2+}, Cr^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+} and Fe^{3+} were 195, 156, 621, 342, 190 and 168 mg/L which were reduced up to the level of 0.0089, 0.1390, 0.3510, 0.0390, 0.0242 and 0.3397 mg/L, respectively in treated samples. This significant removal of heavy metal ions indicates a remarkable efficiency of calcium carbonate as adsorbent. The adsorption capacity of calcium carbonate was calculated, which were found 400-1500 mg/g, while the effect of initial metal ion concentrations on the adsorption process was not pronounced. It is concluded that this treatment method may holds good in order to reduce metals ions concentration in industrial effluents.

Key words: Calcium carbonate, Adsorption capacity, Heavy metals, Industrial effluents

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1. Introduction

Heavy metals are regarded such elements which have atomic weights in the range of 63.5 and 200.6 and specific gravity more than 5. Rapid industrialization and urbanization has resulted in accumulation of heavy metals in the environment due to their waste disposal without any treatment. Various industries such as metallurgy, battery manufacturing, metal plating, fertilizer production, mining, textile dyeing, etc. are major contributors to enhance the concentration of heavy metals in the environment and are responsible for heavy metal contamination [1-6]. Most of the heavy metals have no known biological function in living organisms, while some of them such as Cu, Zn and Ni are thought to be essential at low concentrations for functioning of body but are toxic when increased beyond the permissible limit. Removal of heavy metals has been a severe problem for environmentalists. The elevated concentrations of heavy metals in industrial effluents ultimately contaminating soil and ground water and entering in food chain ultimately affect human beings. Contamination of water by toxic heavy metals is one of the major problems facing the world today, metals can directly or indirectly damage DNA that means an increased risk of cancer called Genotoxicity, while other adverse effects are that these metals may enter in food chain, ingested through food and accumulated, causes health problems such as anemia, kidney disorder, failure in nervous system, high blood pressure, etc. These heavy metals not damage the human beings but also affect plant tissues [7-8]. Metals in solution may be in the form of free ions, soluble salts, associated ion with ligands or ion bound to a particulate matter. Drinking water is mainly contaminated due to the presence of toxic metal ions. Various techniques have been employed for the removal of these ions from the polluted water such as chemical precipitation [9], ion- exchange [10], Phyto-extraction [11] and biosorption [8]. Most of the methods become ineffective and uneconomical when the concentrations of heavy metals are raised 10 -100 times then the permissible limits which is mostly less than 1 mg/L. The development of procedures and protocols which can remove toxic metals from water has remained a focus for last several decades. Adsorption of heavy metals using Calcium carbonate ($CaCO_3$) is an effective technique to remove the heavy metals from water samples. Many researchers have used natural lime stone for the removal of toxic metal ions from polluted water [12-17] and have reported that $CaCO_3$ is an effective material for the treatment of water contaminated with heavy metal ions and have highest removal efficiency for heavy metals [18-19]. It was reported that lime stone samples containing impurities such as silica, iron/ aluminium oxide and different kinds of clay minerals demonstrated enhanced sorption capacity [1].

Adsorption is relatively suitable technique which can be used to reduce the load of heavy metals in the wastewater, since adsorbing materials have metal binding capacity. The major advantage of adsorption over conventional treatment include, low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement and regeneration of sorbent and possibility of metal recovery. The focuses on the potential of a wide variety of low cost adsorbents for the removal of heavy metals require less prior processing, abundantly available in nature, a byproduct of waste material of another industry [7-8].

According to literature survey so for very little references are still available highlighting the removal of heavy metals by calcium carbonate as an adsorbent. During the present study precipitated $CaCO_3$ was taken in a 60 cm long glass column of 8 mm diameter. The $CaCO_3$ bed was 30 cm while the concentration of Zn(II), Cd(II), Cu(II), Cr(III), Fe(III) and Pb(II) metal solutions were 0.003 M. After passing through adsorbents, the eluted solutions were analyzed by atomic absorption spectrophotometer in order to calculate the removal efficiency.

2. Materials and methods

2.1. Chemical and material

The present research work was carried in the laboratories of Department of Chemistry, The University of Faisalabad, Pakistan. The chemicals used during the entire study were of analytical grade while properly washed and oven dried Pyrex glass apparatus was used during the present study. The aqueous solutions of heavy metals were prepared by dissolving the salts of metals in double distilled water. The salts used for solution were $FeCl_3.6H_2O$, $Pb(CH_3COO).3H_2O$, $CrCl_3.6H_2O$, $Cd(NO_3).4H_2O$, $Zn(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$. The concentration of each solution was 0.003 M/L. Pure $CaCO_3$ (precipitated) in powdered form was procured from the local market. The adsorbent was pre dried in oven before filling the column.

2.2. Continuous flow column

The sample solution of heavy metals were percolated through Pyrex glass columns having length of 60cm and internal diameter was 8 mm and glass wool was used as a bed then calcium carbonate was filled in column which act as an adsorbent. The aqueous solution of each heavy metal was then passed in column at a speed of 4mL/minute.

2.3. Analysis of heavy metals

Nov Aa 400 Analytik Jena, Germany Atomic Absorption Spectrometer equipped with an air acetylene flame, controlled with computer was used to investigate the concentration of each metal ion after treatment. The hollow Cathode Lamps for Zn, Pb, Cd, Fe, Cu and Cr were used at a specific wavelength, while slit was 0.2 nm [8].

2.4. Adsorption capacity measurement

The absorption capacity of the calcium carbonate was measured using following relation;

$$q = V(C_i\text{-}C_f)/M$$

Where, q, V, C_i, C_f and M are representing the absorption capacity, volume of sample, initial concentration, final concentration and amount of adsorbent used [8].

3. Results and Discussion

3.1. Absorption of heavy metals

The results revealed that $CaCO_3$ significantly adsorbed heavy metal ions form aqueous solution. The concentration of heavy metals ions such as Fe^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} are shown in Table 1 before and after treatment while Fig. 1 depicts the column treatment. The concentrations of heavy metals ions such as Fe^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} were 168, 156, 190.5, 159.9, 621 and 342 mg/L and after adsorption reduced to the level of 0.339, 0.139, 0.024, 0.008, 0.351 and 0.002 mg/L, respectively. More than 99% reduction of all heavy metal was found in treated sampled when analyzed by AAS. Individually, the observed reduction of metal ions such as Fe^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+} were found to be 99.79%, 99.91%, 99.98%, 99.99%, 99.94% and 99.98%, respectively. The adsorption capacities of $CaCO_3$ in order to reduce the heavy metal ions form aqueous solution were found more pronounced than previous study reported the use of $CaCO_3$–maltose hybrid materials for metal ion adsorption [20]. However, authors reported that $CaCO_3$ showed a good metal binding capability for heavy metals ions and can be used an effective alternative from real industrial wastewater metal removal. In the present study, the higher adsorption capacity of $CaCO_3$ is attributed due to the differences between metal sorption capacities and affinity of $CaCO_3$ adsorption. Furthermore, the radius of cations as well as electronegativity may also affect the adsorption behavior of certain ions. It is well known that smaller radius ions adsorbed strongly and the metals of higher electronegativity can adsorb more easily and vice versa. The solubility is another factor that may affect the adsorption capacity [20].

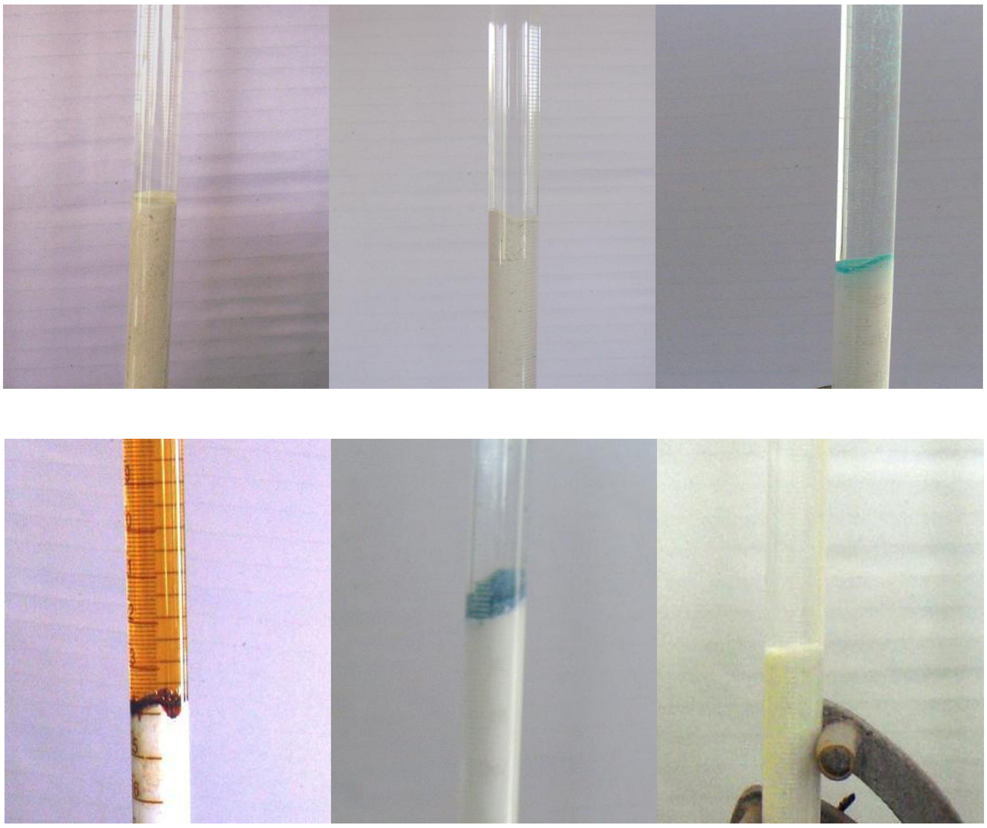
3.2. Adsorption capacity of calcium carbonate and effect of initial concentration

The absorption capacities of $CaCO_3$ of heavy metal ions are shown in Table 2. Calcium carbonate showed a considerable higher absorption capacities such as 502.98, 467.58, 569.92, 1551.62 and 1068.62 mg/g for the removal of heavy metals ions (Fe^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}) form aqueous solution, respectively. The trend in adsorption capacities of was found as; $Pb^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+} >$.

Table 1: Concentration of heavy metals before and after adsorption on calcium carbonate (adsorbent)

Ions	Conc. before adsorption (mg/L)	± SD	Conc. after adsorption (mg/L)	± SD
Fe^{3+}	168	8.40	0.3397	0.020
Cr^{3+}	156	7.80	0.1390	0.008
Cu^{2+}	190.5	9.53	0.0242	0.001
Zn^{2+}	195.9	9.80	0.0089	0.001
Pb^{2+}	621	12.5	0.3510	0.021
Cd^{2+}	342	10.80	0.0390	0.002

Cd^{2+} **Pb^{2+}** **Cr^{3+}**



Fe^{3+} **Cu^{2+}** **Zn^{2+}**

Fig. 1. Column showing the adsorbing material and adsorption pattern of heavy metal ions

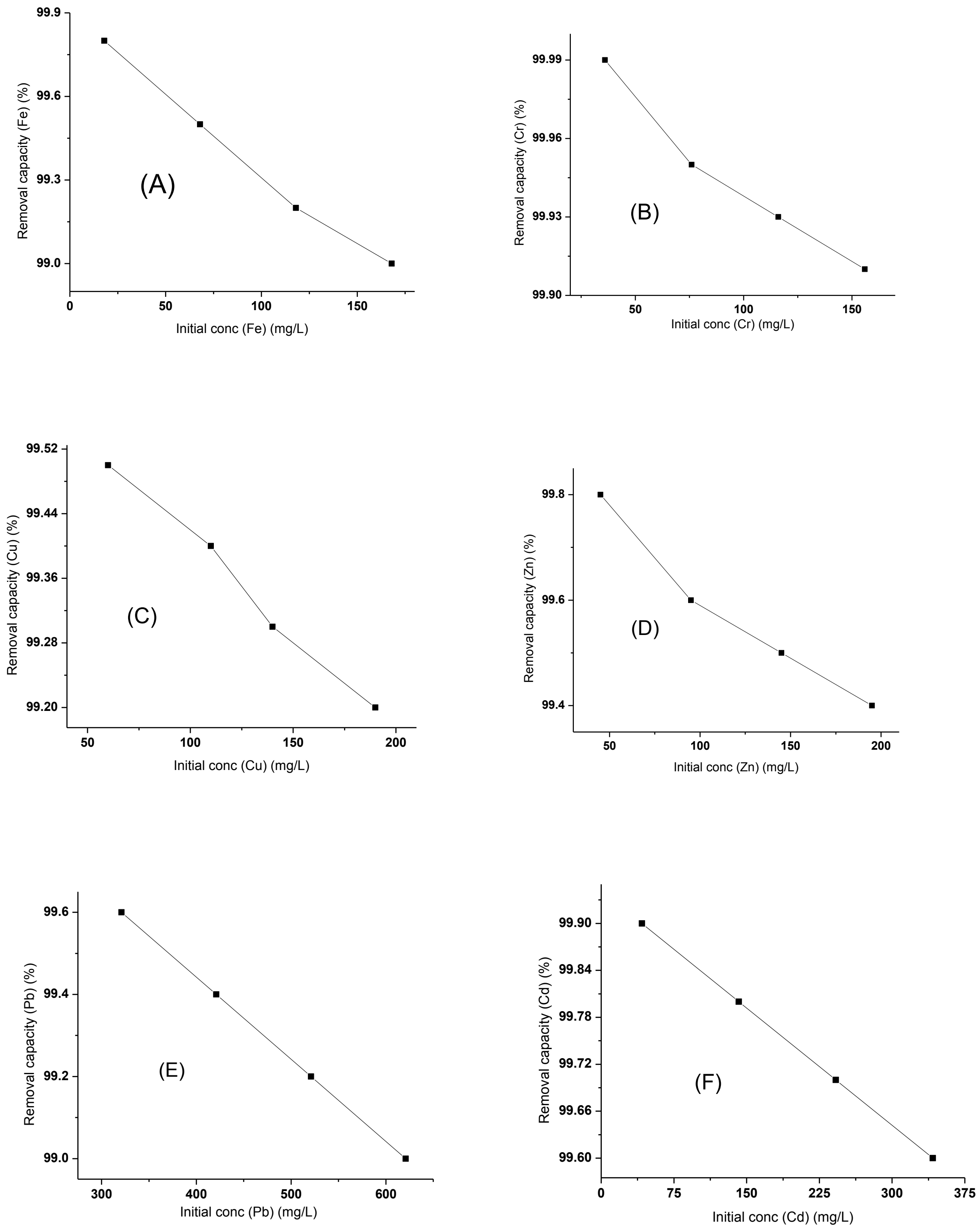


Fig. 2: Initial metal concentration effect on adsorption on calcium carbonate

Table 2. Adsorption capacity of calcium carbonate of heavy metals ions (Fe^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Pb^{2+} and Cd^{2+}) from aqueous solutions

Ions	Ci (mg/L)	Cf (mg/L)	V (mL)	M (g)	q (mg/g)
Fe^{3+}	168	0.3397	30	10	502.9809
Cr^{3+}	156	0.139	30	10	467.583
Cu^{2+}	190	0.0242	30	10	569.9274
Zn^{2+}	195	0.0089	25	8	609.3472
Pb^{2+}	621	0.351	20	8	1551.623
Cd^{2+}	342	0.039	25	8	1068.628

Ci = initial concentration, Cf = final concentration, V = volume of sample, M = amount of adsorbent used and q = adsorption capacity

These different absorption capacities might be due to various factors such as solubility, cationic size, electronegativity, affinity of adsorbent, etc. The responses of absorption of different heavy metal ions on $CaCO_3$ are indicated in Fig. 2 and at lower metal initial concentration, marginally higher adsorption was observed. Furthermore, the ability adsorption of Pb^{2+} ion was significantly higher than other metal ions followed by Cd^{2+} ions. The percentage removal decreases with the increase in initial heavy metal concentration. The percentage removal of Fe^{3+} was almost complete (nearly 100%) at the initial metal ions concentration of 18 mg/L/10 g $CaCO_3$ adsorbent dose and this adsorption reduces to 99% at initial concentration of 168 mg/L. Similarly, the absorptions of Cd^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} were observed 99.99%, 99.2%, 99.7%, 99.6% and 99.9% for initial metal concentrations of 36, 60, 155, 321 and 42 mg/L, while reduces to 99.91, 99.5, 99.4, 99 and 99.6% of Cd^{2+}, Zn^{2+}, Cu^{2+}, Fe^{3+} and Cr^{3+} for the initial concentrations of 156, 190, 195, 621 and 342 mg/L, respectively. A marginally higher adsorption at lower concentration may be due to the high collision efficiency between the metal ions and the adsorbent. At higher concentration, there may be lack of available sites for adsorbing metal ions on the adsorbent surfaces and may prevent further adsorption of metal ions [20-21].

4. Conclusion

It is concluded that calcium carbonate may act as an efficient adsorbing material for the adsorption of heavy metals ion from aqueous solution. The calcium carbonate may reduce the level of heavy metals more than 99%. From results, it is suggested that this adsorbing material can be effectively used for the removal of heavy metal ions from any industrial effluent. Furthermore, there is a need to explore the effect of different operating parameter such as pH, adsorbent dose, loading volume and mechanism of action.

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