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Determination of Breakthrough Curves for the Uptake of Fe^{3+} Using Magmatic Rock Material in Fixed Bed Column

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Abstract-The breakthrough curves of the particles of magmatic rock to uptake Fe^{3+} ions from aqueous solution were investigated using a fixed-bed sorption column. The effect of inlet Fe^{3+} concentration, feed flow rate, bed height, initial solution pH and particle size on the breakthrough characteristics of the sorption system were investigated. The highest experimental bed capacities for Fe^{3+} ions was obtained to be 3.65 $mg.g^{-1}$ at inlet Fe^{3+} concentration of 75 ppm, bed height of 5 cm and flow rate of 5 $mL.min^{-1}$, pH of 5 and particle size of 0.25-0.5 mm, respectively. The results indicated that magmatic rock material is a suitable sorbent for the uptake of Fe^{3+} ions from an aqueous solution.

Keywords: Magmatic rock, Fe^{+3}. Fixed bed, Flow rate and Bed Depth

1.Introduction

Excessive concentrations of Fe^{+3} in public water supplies causes turbidity, unpleasant taste and odor. It imparts a brownish color to laundered cloths and stains plumbing fixtures. It also causes difficulties in distribution systems by supporting the growth of iron bacteria, resulting in the clogging of pipes (1). Therefore, the presence of Fe^{+3} is objectionable in certain industries such as food, textile and paper (2). Up to now, various traditional treatment technologies including chemical precipitation, filtration, ion exchange and activated carbon adsorption on a solid heterogeneous surface are widely applied (3-5). These methods, however, display one or more limitations, such as ineffective, expensive, generation of secondary pollution and narrow appliance range (6-8).

Magmatic rock is an economical rock, and is included to light concrete category (9). These rocks are widely used as building stone in low storeyed buildings and especially in historical building in the past (10).

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One of the main advantages of Fe^{+3} removal using magmatic rock over the other chemical treatment methods is that any chemical sludge does not produce after sorption. The purpose of this study is to investigate the performance of magmatic rock particles in the removal of Fe^{+3} from aqueous solutions in a fixed-bed coloumn. The effect of influent Fe^{+3} concentration, pH, particle size, bed height, and flow rate on the column performance and shape of the breakthrough curves was evaluated. Kinetic column model (Bed depth service time (BDST)) was applied to describe the dynamic performance of the sorption process.

2.Material and Methods

2.1. Sorbent preparation

The magmatic rock particles were grounded in a blender and sieved to obtain the particle sizes such as 0.25<x<0.5, 0.5<x< 1 and 1<x< 2 mm. Magmatic rock samples were washed with distilled water and then dried at 298 K during two weeks. The samples of 7 g were taken for sorption studies Fe^{+3} solutions were prepared by diluting 483 mg/L of $FeCl_3 \cdot 6H_2O$ (Merck) stock solution with deionized water to a desired concentration range between 20 and 75 ppm.

2.2. Fe^{+3} Analysis

A sample of 5 ml that has a concentration less than 20 mg Fe^{3+}/100 mL was added 10 ml of 1% sulfosalicylic acid and a few drops of 25% aqueous ammonia solution to keep the value of pH between 2.1 and 3.3, and then diluted to 50 ml with distilled water. The content of Fe^{+3} was determined by titration with 0.05 M EDTA solution. 1 ml, 0.05 M EDTA solution is equivalent to 2.792 mg Fe^{+3} (11).

2.2. Column experiments

Continuous flow sorption experiments were conducted in teflon columns of 1 cm i.d. and 5, 10, 15 and 20 cm heights. Fe^{+3} solution having an initial concentration of 50 ppm was pumped upward through the column at a desired flow rate by a peristaltic pump. Operation of the column was stopped when the effluent Fe^{+3} concentration equals influent Fe^{+3} concentration. The amount of metal retained in the column depends on the influent metal concentration and can be calculated from the area above the breakthrough curve (Eq.1).

$$q = \frac{C_o Q}{m \cdot 1000} \int_0^t \left(1 - \frac{C_t}{C_o}\right) dt \qquad (1)$$

where q represents the amount of metal retained (mg of iron per g of sorbent), C_t and C_o are the Fe^{+3} concentrations at the column effluent and influent (ppm) respectively, Q is the flow rate (mL/min), m is the mass of sorbent in the column (g) and t is the sorption time (min).

3. Results

3.1 The Effect of experimental conditions on the breakthrough curve

3.1.1. Effect of Initial Iron Concentration

The effect of influent Fe^{+3} concentration on the shape of the breakthrough curves was shown in Fig. 1. As shown in Fig. 1 , in the interval of 75 min, the value of C_t/C_o reached 0.065, 0.30 and 0.52 when influent concentration was 20, 50 and 75 ppm respectively. It is illustrated in Fig.1 that the breakthrough time decreased with the increase of influent Fe^{+3} concentration. At lower influent Fe^{+3} concentration, breakthrough curve was dispersed and breakthrough occurred slower. As influent concentration increased, sharper breakthrough curves were observed. These results demonstrate that the change of concentration gradient affects the saturation rate and breakthrough time (12).

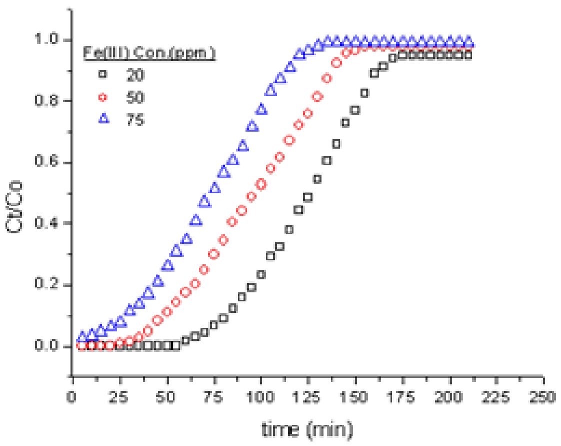

Fig 1. Experimental breakthrough curves of Fe^{+3} as a function of inlet Fe^{+3} concentration (T 15°C, pH 4, flow rate 5 $mL.min^{-1}$, bed depth 5cm, particle size 0.25-0.5 mm)

3.1.2. Effect of Flow Rate

The flow rate was changed in the range of 6 to 12 $mL.min^{-1}$ while the concentration of Fe^{+3} in influent was kept constant at 50 ppm. The obtained results show that the adsorption of Fe^{+3} on the the particles of magmatic rock was strongly influenced by the flow rate. All the breakthrough curves had a similar shape.

The breakthrough curves shifted to the origin with increasing flow rate, and an earlier breakthrough time and saturation time were observed for a higher flow rate. As shown in Fig. 2, in the interval of 75 min, the value of C_t/C_o reached 0.29, 0.89 and 0.98 when flow rate was 6, 9 and 12 $mL.min^{-1}$, respectively.

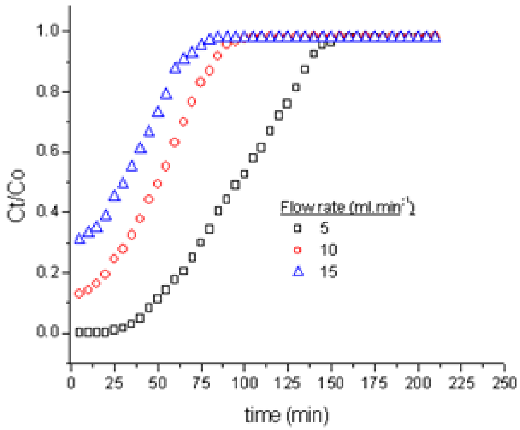

Fig 2. Experimental breakthrough curves of Fe^{+3} as a function of flow rate (T 15°C, pH 4, Co 50 ppm, bed depth 5 cm, particle size 0.25-0.5 mm).

3.1.3. Effect of Bed Depth

Because of the pressure drop and the handling problems of the smaller particle size <0.25-0.5 mm in the column studies, the particle sizes of 1-2 mm were used to compare C_t/C_o with adsorbent capacities for the bed depths of 5, 10,15 and 20 cm. Fig. 3 shows the breakthrough profile of Fe^{+3} sorption at different bed heights.

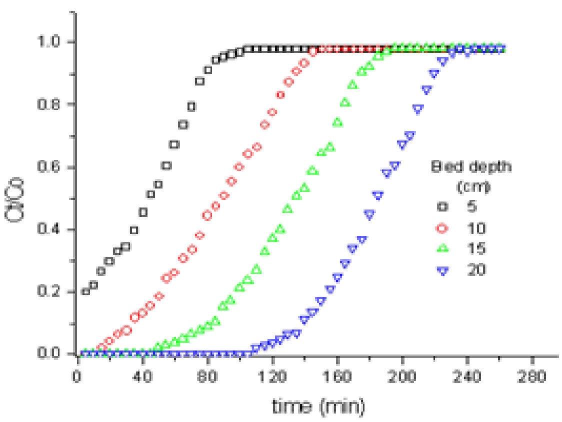

Fig 3. Experimental breakthrough curves of Fe^{+3} as a function of bed depth (T 15°C, pH 4, Co 50 ppm, flow rate 5 $mL.min^{-1}$, particle size 1-2 mm).

For the different four bed depths used, as the bed depth increases, the quantity of the removed Fe^{+3} concentration increases which is also illustrated by the service time change. As shown in Fig. 4, in the interval of 75 min, the value of C_t/C_o reached 0.74, 0.25, and 0.046 when bed depth was 5, 10 and 15, respectively.

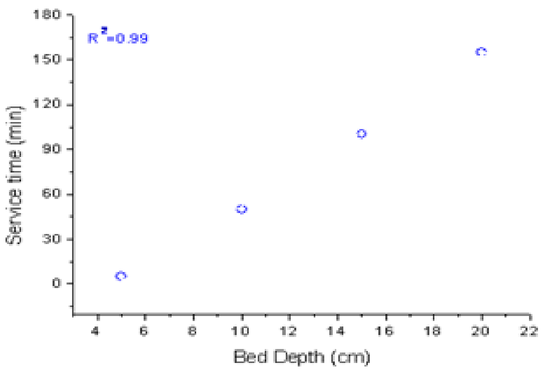

Fig 4. BDST model (Co 50 ppm, pH 4, flow rate 5 $mL.min^{-1}$).

The BDST is one of the most widely used models that describe the heavy metal adsorption using a column system. It assumes that the rate of sorption is governed by the surface reaction between the sorbate and the unused capacity of the sorbent. It does not take into account the intraparticle mass transfer resistance as well as the external film resistance where the sorbate is directly sorbated onto the surface of the sorbent (13).

It is given by the Eq(2).

$$t_s = \frac{N_o Z}{C_o U_o} - \frac{1}{k_{ads} C_o} \ln\left(\frac{C_o}{C_b} - 1\right) \qquad (2)$$

where t_s is the service time (min), C_o and C_b are the influent concentration and the breakthrough effluent concentration (mg/L), Z is the bed depth (cm), U_o is the linear flow rate ($cm.min^{-1}$), k_{ads} is the sorption rate constant that describes the mass transfer from the liquid phase to the solid phase ($L.mg^{-1}$ min^{-1})), and No is the dynamic bed capacity ($mg.L^{-1}$). The plot of service time against bed depth at a flow rate of 5 $mL.min^{-1}$ was linear indicating the validity of BDST model as seen Fig.4. The rate constant, k_{ads} is a measure of the rate transfer of metal solution from the fluid phase to the solid phase. For Fe^{+3}, the values of No and k_{ads} were 3466 $mg.L^{-1}$ and 0.000583 $L.mg^{-1}.min^{-1}$, respectively. A larger value for k_{ads} implies that even at lower bed heights, breakthrough will occur at a later time whereas a smaller k_{ads} value needs a higher bed height to avoid breakthrough (14).

3.1.4. Effect of pH

Solution pH has more influence to uptake Fe^{+3} ions in the fixed bed. It influences both the sorbent surface metal binding sites and the metal chemistry in water. When pH of feed solution was changed from 1.7 to 4, the highest sorbent capacity and the longest breakthrough time was achieved at pH 4. As shown in Fig. 5, in the interval of 75 min, the value of C_t/C_o reached 0.99, 0.53 and 0.29 when pH value of the solution was 1.8, 3 and 4, respectively.

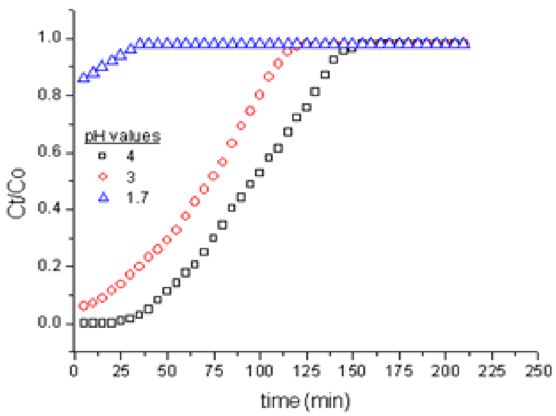

Fig. 5. Experimental breakthrough curves of Fe^{+3} as a function of pH of solution (T 15°C, bed depth 5 cm, Co 50 ppm, flow rate 5 $mL.min^{-1}$, particle size 0.25-0.5 mm).

At pH between 3 and 4, there are three species present in the solution as suggested by Araujo et al. (15,13). The dominant species between pH 3 and 4 were $Fe(OH)^{2+}$, $Fe(OH)^{+}_{2}$ and $Fe(OH)_3$. It was thought that these species are sorbated electrostatically and showed chemical interaction on the surface of the shells. At low pH, the surface charge becomes positive due to high concentration of H_3O^+ ions. At low pH, the very low sorption effectiveness is likely due to competition for binding sites with protons.

3.1.5. Effect of Particle Size

The particle sizes were 0.25-0.5, 0.5-1 and 1-2 mm, while the bed depth, influent Fe^{+3} concentration and pH were kept constant at 4 cm, 50 ppm and 4, respectively. The breakthrough curves concerning with particle size are given in Fig. 6. An increase in the particle size appeared to increase the sharpness of the breakthrough curve. Furthermore, the sorption capacity for the larger particle size is lower than that for smaller one.

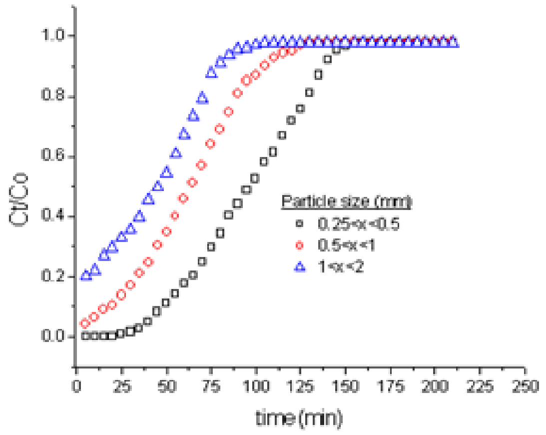

Fig. 6. Experimental breakthrough curves of Fe^{+3} as a function of particle size (T 15°C, bed depth 5 cm, Co 50 ppm, flow rate 5 $mL.min^{-1}$, pH 4).

A rapid decrease in the column sorption capacity with an increase in the particle size was observed. As shown in Fig. 6, in the interval of 65 min, the value of C_t/C_o reached 0.29, 0.57 and 0.74 when the particle size was 0.25-0.5, 0.5-1 and 1-2 mm, respectively.

5. Conclusion

The particlesof magmatic rock were used to define the experimental sorbent capacities in a fixed bed column. The C_t/C_o are a function of the adsorption time, sorbent dosage, sorbate concentration, sorbent particle size, pH and bed depth. The removal of Fe^{+3} in a packed bed system using the particles of magmatic rock as an sorbent is an effective and feasible method. The shape of the breakthrough curve and the Fe^{+3} uptake capacity of the magmatic rock bed is strongly dependent on the bed height, flow rate, and influent concentration, pH and particle size. A longer breakthrough and exhaustion time occurred at a higher bed height, a lower flow rate, and lower influent concentration, lower pH value and particle size. At the optimum condition, the sorption capacity value is 3.65 mg Fe^{+3} per g magmatic rock with time of breakthrough and exhaustion at 45 min and 115 min, respectively. The BDST model was used in the determination of the kinetic column parameters. It provided a good correlation in the prediction of the breakthrough time due to its acceptable R^2 values (0.99).

6.References

[1] Y. Onganer, and C. Temur, "Adsorption dynamics of Fe+3 from aqueous solutions onto activated carbon," J. Colloid Interface Sci, vol. 205, pp.241–244.1998

[2] Y. Sag, and T. Kutsal, "Fully competitive biosorption of chromium (VI) and iron (III) ions from binarymetal mixtures by R. arrhizus: use of the competitive Langmuir model," Process Biochem, vol 31, pp. 573–585.1996

[3] M. Malki, E. G. Toril, J. L. Sanz, F. Gomez, N. Rodriguez, and R. Amils, "Importance of the iron cycle in biohydrometallurgy," Hydrometallurgy, vol 83, pp. 223-228. 2006

[4] E. Khan, M. Li, and C.P. Huang, "Hazardous waste treatment technologies," Wat. Env. Res, vol. 79, pp. 1858-1902. 2007

[5] Z. Aksu, and I. Alperisoglu, "Removal of copper ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp," Process Biochem, vol.40, pp.3031-3044. 2005

[6] E. Pehlivan, and G. Arslan, "Removal of metal ions using lignite in aqueous solution-low cost biosorbents," Fuel Process Technol, vol. 88, 99-106. 2007

[7] V.K. Gupta, and I. Ali, "Utilisation of bagasse fly ash (a sugar industry waste) for the removal of copper and zinc from wastewater," Sep. Purif. Technol. vol.18, pp 131-140. 2000.

[8] V.K. Gupta, and A. Rastogi, "Biosorption of lead(II) from aqueous solutions by nonliving algal biomass *Oedogonium* sp. and *Nostoc* sp.-a comparative study," Colloids Surf. B, vol.64, pp. 170-178. 2008

[9] A. C. Aydin, M. B. Karakoç, O. A. Düzgün and M. S. Bayraktutan, "Effect of low quality aggregates on the mechanical properties of lightweight concrete" Scientific Research and Essays, vol 5, pp. 1133-1140. 2010

[10] Mustafa Korkanc, 'The Effect of Geomechanical Properties of Magmatic rocks on Their Usage as Building Stone: Nevşehir, *Jeoloji Mühendisliği Dergisi, vol. 31,* pp. 49-60 2007

[11]H. Gulensoy, "Komplexometrinin esasları ve komplexsometrik titrasyonlar, Fatih Yayınevi", pp.109-111.1984

[12] J. Goel, K. Kadirvelu, C. Rajagopal, and V.K. Garg, "Removal of lead (II) by adsorption using treated granular activated carbon: batch and column studies," J. Hazard. Mater. B, vol.125, pp. 211-220. 2005

[13] S. Qaiser, A. R. Saleemi, and M. Umar, "Biosorption of lead from aqueous solution by Ficus religiosa leaves: Batch and column study," Journal of Hazardous Materials, vol.166, pp. 998-1005. 2009

[14] K.Vijayaraghavan, J. Jegan, K. Palanivelu, and M.Velan, Removal of nickel (II) ions from aqueous solution using crab shell particles in a packed bed up-flow column. Journal of Hazardous Materials, B, vol.113,pp.223–230.2004

[15] G.C.L.Araujo, S.G. Lemos, A.G. Ferreira, H.Freitas, A.R.A. Nogueira, "Effect of pre-treatment and supporting media on Ni(II), Cu(II), Al(III) and Fe+3 sorption by plant root material. Chemosphere vol.68, pp.537-545. 2007