LEACHATE TREATMENT BY HEAT TREATED ZEOLITE MEDIA

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Introduction

Zeolite media consist of dehydrated aluminium silica. Silica atom and Aluminium in Zeolite forms a tetrahedral structure and both shares an Oxygen atom [1]. Due to this structure it inherently contains numerous pores. It is non-toxic to humans and exhibit high temperature stability for regeneration and also used as a common catalyst for ion exchange processes [2]. Its capacity as adsorbent is widely influenced by the large number of capillaries within a single particle. The surface available for adsorption includes the surface of the pores in addition to the external surface area of the particle. The pore surface area exceeds the surface area of the particle. Further heat treatment was shown to increases the number of pores on the Zeolite [3]. Granular activated carbon (GAC) and Zeolite are suitable for removing low concentration Chemical Oxygen Demand (COD) and Ammonical Nitrogen (NH₄-N) from effluents [4, 5]. Earlier researches by Rozic et. al. [6] conducted on NH₄-N removal using zeolite batch and column studies have shown efficiency value for NH₄-N of 61.1 wt%, and Sarioglu [5] has shown the overall ion adsorption capacity of 164.62 meq per 100 gram of zeolite. However, the actual removal mechanism of Iron (Fe³⁺), NH₄-N and COD on a typical leachate from landfill has not yet been studied extensively. This work was conducted to study pollutant removal capability of heat treated zeolite media.

The theoretical adsorption capacity of zeolite for Iron (Fe³⁺), COD and NH₄-N is determined by calculating its adsorption isotherms. The amount of material adsorbed is determined as a function of concentration at a constant temperature.

Experimental

Zeolite used in this research comprises the empirical formula $[CaNa]_8Al_8Si_{40}O_{96}24H_20$. It was grounded and sieved to 2.00 - 2.36 mm particle size and washed with distilled water to remove impurities and small particles. It was then dried at 105 °C for 24 hours to remove moisture. The raw zeolite used had a mineralogical chemical content and specification of SiO₂ - 62.75 %, Al₂O₃ - 13.63 %, theoretical exchange capacity 110 - 120 meq/100 gram, grain size 2 - 4 mm and surface area 68 – 110 m²/gram. Heat treated zeolite was prepared by heating natural zeolite to 300 °C for 48 hours. Eight 250 ml conical flask containing zeolite samples and 100 ml leachate solution were employed. The orbital shaker model Bioscience 74578 was used for agitation purpose to keep the zeolite in suspension. The Whatman 90mm filter paper with the assistance of a vacuum pump was used for effluent filtration. COD was determined by Reactor Digestion and Colorimetric Spectrophotometer (HACH DR/2010), NH₄-N was analysed using standard Nesslerisation Method (HACH DR/2010) Spectrophotometer. Heavy metal Iron (Fe³⁺) was quantified by utilizing Shimadzu AA-660 Atomic Absorption Spectrophotometry technique.

Batch study

In the batch studies the effect of agitation time on Iron Fe³⁺, NH₄-N and COD adsorption and pollutant (Fe³⁺ - 1.70 mg Γ^1 , NH₄-N - 702 mg Γ^1 and COD - 516.8 mg Γ^1) removal capability of natural and heat treated zeolite was investigated. In order to determine the optimum agitation time, 10 gm of natural and heat treated zeolite was added to 100 ml leachate in a 250ml conical flask. Agitation speed 350 rpm was employed. 2.5 ml of reactant were extracted from the conical flasks kept on the agitator at time intervals of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60 minutes. The sample was immediately filtered using the Whatman 90 mm filter paper and analysed. The experiments were repeated thrice to obtain consistent results at room temperature $25\pm2^{\circ}$ C.

Results and Discussion

Figure 1 illustrates the optimal agitation time for removal of pollutants. Maximum pollutant removal was attained at 40 minutes with 350 rpm. The initial pollutant concentration provides the necessary driving force to overcome all mass transfer resistance between the aqueous and solid phase. The removal of pollutants was high in the initial 10 minutes of the experiment, which was found to level off and eventually approached zero. These changes in the rate of removal are due to the availability of vacant sites on the zeolite and the high solute concentration gradient in the initial phase of experiment. Which subsequent adsorption of the pollutant the vacant site decreased significantly. A decreasing removal rate, particularly towards the end of experiment, indicates a possible monolayer of pollutant ions on the outer surface and pores of the zeolite. Continuous agitation results in pore diffusion onto the inner surface of

zeolite particles through the monolayer film. Heat treated zeolite achieved a removal capacity almost 10 times greater for heavy metal Fe³⁺ and COD (Figure 2, 3). This is due to the formation of extra fine pores onto the natural zeolite during the heat treatment process. The removal of NH₄-N was comparably lower (Figure 4).



Figure 1. Optimal agitation time and pollutant removal efficiency for heat treated zeolite at 350rpm



Figure 2. Comparison of zeolite media for Fe³⁺ removal

The equilibrium removal of the pollutant ion can be mathematically expressed in terms of adsorption isotherms, $Q = K_f C_e^{1/n}$. The Freundlich model expresses the quantity of adsorbate taken up by the adsorbent as a function of initial pollutant concentration C_e [7].

The large K_f (Table 1) with relatively similar 1/n indicates that the heat treatment on zeolite media did not change the adsorption mechanism. The K_f value indicates high adsorption potential due to existence of extra pores. It was found that NH₄-N exhibits less adsorption capability due to its larger molecular size to form a monolayer on the zeolite media. Due to the comparable nature of the pore size and the molecular size of Fe³⁺ zeolite forms an excellent absorbent for Fe³⁺ and COD.



Figure 3. Comparison of zeolite media for COD removal



Figure 4. Comparison for Zeolite Media for NH₄-N Removal

POLLUTANT	Zeolite Type	\mathbb{R}^2	1/n	$\mathbf{K}_{\mathbf{f}}$
FERUM (Fe ³⁺)	Natural	0.9922	0.707	0.6080
	Heat Treated	0.9938	0.727	0.8060
COD	Natural	0.9872	0.653	0.5020
	Heat Treated	0.9978	0.662	0.7233
NH ₄ -N	Natural	0.9827	0.442	0.4054
	Heat Treated	0.9912	0.469	0.6133

Table 1. Freundlinch models parameter for best fit and corresponding correlation coefficients

Conclusion

Heat treated Zeolite was found to exhibits high adsorption capability for Fe^{3+} and COD removal. Larger values of 1/n shows that a weak bond (physical bond) was formed between the pollutants and adsorbent

which can be removed easily (regenerable). Heat treated zeolite was found to be 10 times more efficient than natural zeolite and could be a potential solution for leachate treatment.

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