



## A new approach to evaluate natural zeolite ability to sorb lead (Pb) from aqueous solutions

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Lead (Pb) is a hazardous pollutant commonly found in aquatic ecosystems. Among several methods available, the addition of sorbent amendments to soils or sediments is attractive, since its application is relatively simple, while it can also be cost effective when a low cost and re-usable sorbent is used; e.g. natural zeolites. Zeolites are crystalline aluminosilicates with a three-dimensional structure composed of a set of cavities occupied by large ions and water molecules. Zeolites can accommodate a wide variety of cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , which are rather loosely held and can readily be exchanged for others in an aqueous solution. Natural zeolites are capable of removing cations, such as lead, from aqueous solutions by ion exchange. There is a wide variation in the cation exchange capacity (CEC) of natural zeolites because of the different nature of various zeolites cage structures, natural structural defects, adsorbed ions, and their associated gangue minerals. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, such as clays and feldspars, metals, quartz, or other zeolites as well. These impurities affect the CEC even for samples originated from the same region but from a different source. CEC of the material increases with decreasing impurity content. Potentially exchangeable ions in such impurities do not necessarily participate in ion exchange mechanism, while, in some cases, impurities may additionally block the access to active sites. For zeoliferous rocks having the same percentage of a zeolitic phase, the CEC increases with decreasing Si/Al ratio, as the more Si ions are substituted by Al ions, the more negative the valence of the matrix becomes. Sodium seems to be the most effective exchangeable ion for lead. On the contrary, it is unlikely that the potassium content of the zeolite would be substituted. A pretreatment with high concentration solutions of Na, such as 2 M NaCl, can significantly improve zeolite CEC by bringing the material to near homoionic form. pH and temperature are the critical parameters for using natural zeolites as sorbents. Zeolites should not be used in extremely acidic, neither in extremely basic pH conditions, except for very short times. The exchange of Pb, requires low solution pH, to avoid precipitation but not too low because the  $\text{H}^+$  are competitive ions for ion exchange; as a result the zeolite CEC related to Pb removal may be downgraded. If pH enters the basic range (e.g. pH>8), more aquatic complexes with lower positive valence than those prevailing in lower pH are produced; these complexes are less attracted by the negative charged zeolitic matrix. Pb uptake is favored at higher temperatures as ion exchange (including the diffusion of exchangeable ions inside the material and the medium, and vice versa) is an endothermic process. With the increase of temperature there is a decrease in hydration of all available exchangeable cations that eases the movement within the channels of the solid matrix. Additionally, the mobility of the potassium ions, present in the zeolitic material, also increases with the temperature resulting in enhanced CEC.