ZEOLITE BEARING TUFF AS AN ADSORBENT FOR HEAVY METALS REMOVAL FROM AQUEOUS SOLUTIONS AND ACID MINE DRAINAGE

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Abstract

Zeolite bearing tuff (stilbite 27%) from Vetunica deposit, localized in northern marginal parts of the Kratovo-Zletovo volcanic area in Republic of Macedonia was investigated as an adsorbent for removal of copper, zinc, manganese and lead ions from synthetic aqueous solutions and acid mine drainage from SASA lead - zinc mine in Republic of Macedonia.

In order to determine the metals uptake at equilibrium a series of experiments were performed under batch conditions from single ion solutions. Experiments were carried out at different initial concentration of metal ions, at initial pH =3.5, temperature of 20±1˚C and agitation time up to 360 min.

The adsorption isotherm of the metal ions on the adsorbent was determined and correlated with the Langmuir and the Freundlich adsorption isotherm models. The Langmuir isotherm exhibited a better fit for the adsorption data for copper, lead and manganese ions, but adsorption of zinc ions is fitting by the Freundlich isotherm. According to the maximum adsorption capacity (q_e) was determine the selectivity of zeolite bearing tuff for the respective heavy metal ions. The selectivity series was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

The acid mine drainage from Sasa mine, Makedonska Kamenica, Macedonia is with high concentration of heavy metal ions and belongs in V class according to The Standards for Water Quality in the Republic of Macedonia. After treatment with zeolite bearing tuff the results shows that at equilibrium more than 99%, 98 %, 74 % and 66 % of lead, copper, zinc and manganese, respectively , were removed from the acid mine drainage.

The adsorption of copper, zinc, manganese and lead ions from diluted solution and acid mine drainage onto zeolite bearing tuff occurs efficiently.

Adsorbent

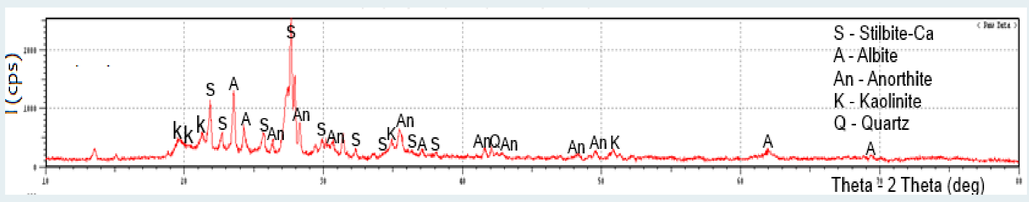
In the recent study for adsorbent is used zeolite bearing tuff that contain stilbite 27 % from Vetunica deposit, localized in northern marginal parts of the well-known Kratovo-Zletovo volcanic area in Republic of Macedonia.

The particle size range of used material was 0.8 to 2.5 mm.

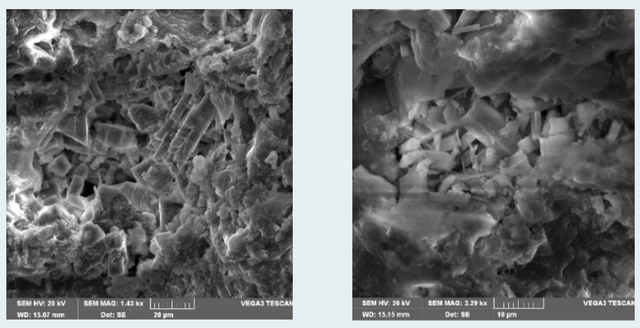
The dominant ion, in the exchangeable position, is K^+ (66.5 meq/100g), followed by Ca^{2+} (21.5 meq/100g), Mg^{2+} (8.5 meq/100g) and Na^+ (3.5 meq/100g). The total cation exchange capacity is 0.94–1.07 meq/g.

Chemical composition (%)									
SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	Na_2O	MnO	P_2O_5	FeO
54,67	20,16	4,86	1,08	2,40	0,45	1,97	0,06	0,24	3,98
Hydrated density(g/cm^3)			Dehydrated density(g/cm^3)				Porosity (%)		
1.72			0.89				48.40		

X-Ray Diffractometer 6100 from Shimadzu was used to investigate the mineralogical structure of the sample. The results shown that present minerals in the sample are stilbite, albite, anorthite, kaolinite and quartz.



The surface morphology of sample was studied using a scanning electron microscope, VEGA3 LMU. The micrographs clearly show a number of macropores and well defined crystals of stilbite in the zeolite structure.



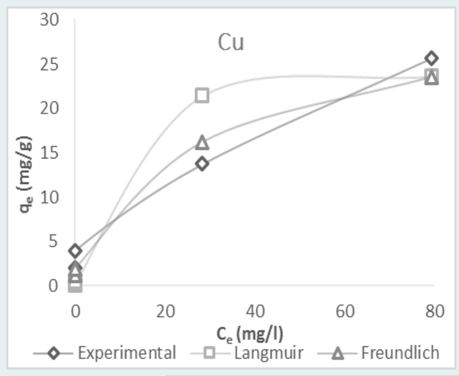
Adsorbate

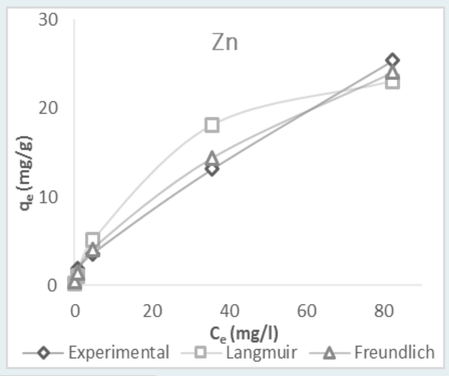
The heavy metals, Cu, Zn, Mn and Pb were used as adsorbate in the recent investigations. For equilibrium experiments, synthetic single component solutions of these metals were prepared by dissolving a weighed mass of the analytical grade salt $CuSO_4.5H_2O$, $ZnSO_4.7H_2O$, $MnSO_4.H_2O$ and $Pb(NO_3)_2$, appropriately, in 1000 ml distilled water. For study acid mine drainage treatment was used drainage water from lead and zinc mine Sasa from Makedonska Kamenica, Macedonia.

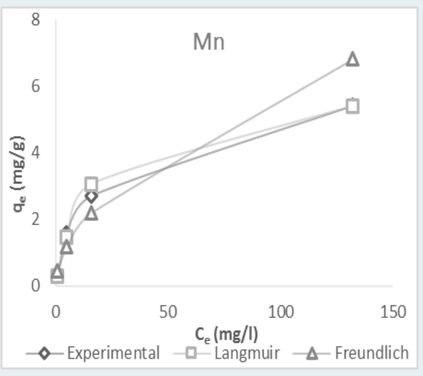
Synthetic solutions

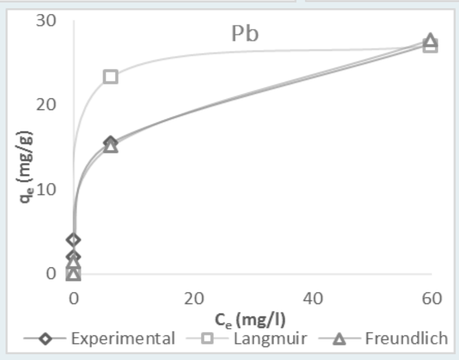
The main objective of the equilibrium studies was to determine the maximum capacity of zeolite bearing tuff towards copper, zinc, manganese and lead removal under the studied conditions.

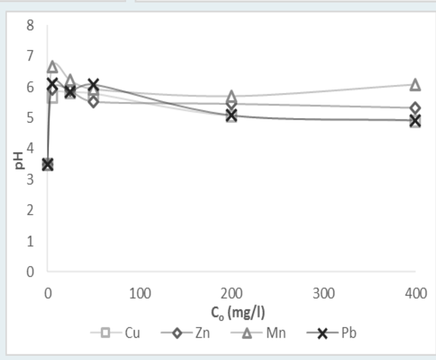
Heavy metal	Experimental		Langmuir				Freundlich			
	Q_e (mg/g)	C_e (mg/l)	q_m (mg/g)	K_l (l/mg)	R^2	R_L	K_f(l/mg)	1/n	n (g/l)	R^2
Cu	25.656	79.3	25.0627	0.2065	0.9155	0.0119	4.7808	0.3646	2.7427	0.7786
Zn	25.408	82.4	29.0698	0.0464	0.845	0,0511	1.6118	0.6128	1.6319	0.9849
Mn	5.416	132.3	6.0386	0.0640	0.998	0.0376	0.4992	0.5349	1.8695	0.9378
Pb	27.224	59.7	27.548	0.8875	0.9937	0.0028	9.3154	0.2667	3.7495	0.7525











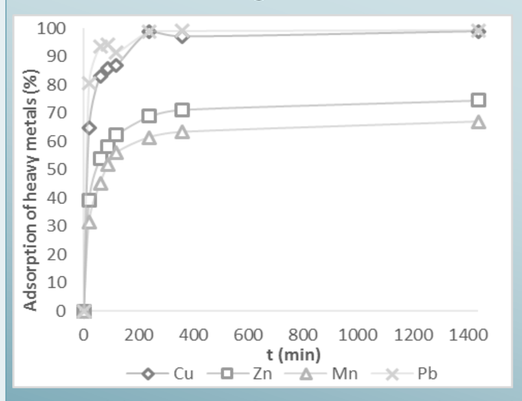
It is concluded that as the initial concentration of metal cations increases, the amount of metal adsorbed per gram of zeolite bearing tuff (q_e) increases.

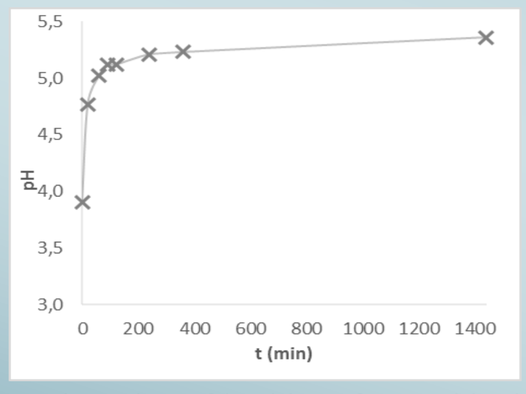
Experimental data were fitted to the Langmuir and Freundlich adsorption isotherms. According to the Freundlich model, values of the heterogeneity factor 1/n, for all these metals, indicate that zeolite bearing tuff is heterogeneou adsorbent. Based on the correlation coefficients (R^2), the adsorption isotherms for Cu, Mn and Pb can be better described by the Langmuir model, but for Zn is better described by Freundlich model. The applicability of the Langmuir isotherm suggests monolayer coverage of the metal ions at the surface of the zeolite bearing tuff or that a similar exchangeable ions with equivalent concentration was exchanged by metal ions. The R_L values show that the behaviour of metal ions adsorption for all studied metals was favourable ($0 < R_L < 1$). The selectivity of used adsorbent was done by comparing the maximum adsorption capacity (q_e) of zeolite bearing tuff and the own unique selectivity series in single component solution was: $Pb^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$.

The equilibrium pH value are greater than the initially adjusted pH values and the difference between equilibrium pH and initial pH exhibits a descending trend with increasing initial metal concentration. According to E. Erdem (2004), natural zeolite has buffer effect and with this results can confirms that zeolite bearing tuff has buffer effect.

Acid mine drainage

According to the results obtained for synthetic acid solutions can be concluded that adsorption of used heavy metal ions onto zeolite bearing tuff at studied conditions occurs efficiently. Upon receipt of such a conclusion, the investigation continues with acid mine drainage taken from Sasa mine, Makedonska Kamenica, Macedonia. From the initial concentration and pH value can be seen that drainage from Sasa mine is acid mine drainage with high concentration of heavy metal ions and belongs in V class according to The Standards for Water Quality in the Macedonia.





Acid mine drainage from SASA mine	Cu (mg/l)	Zn (mg/l)	Mn (mg/l)	Pb (mg/l)	pH
Initial concentration and pH	0,66	2,219	2,053	0.329	3,90
Remain concentration and pH	0,007	0,564	0,678	0.002	5,36

	Classification of water and concentration(mg/l)		
	I-II class	III-IV class	V class
Cu	0.01	0.05	> 0.05
Zn	0.1	0.2	> 0.2
Mn	0.05	1	> 1
Pb	0.01	0.03	> 0.03
pH	6.3-8.5	5.3-6.3	< 5.3

As could be seen from presented results, adsorption of lead ions from acid mine drainage onto zeolite bearing tuff occurs efficiently. It means that more than 99% of lead ions are removing from acid mine drainage. It can be concluded that kinetics of lead adsorption is reasonably fast and after 20 min more than 80 % lead ions were adsorbed. Equilibrium for others studied ions are achieve slowlier. Adsorption of copper, zinc and manganese ions at equilibrium are 98.9 %, 74.5 % and 66.9 % respectively.

As mentioned above, zeolite bearing tuff has buffer effect. It is confirm with obtained result, pH from 3.90 increase to 5.36. According to pH value, acid mine drainage after treatment belong to III-IV class. The quality of acid mine drainage after treatment for lead and copper concentration satisfy quality of I-II class, for manganese III-IV class and for zinc the concentration is still high and belongs to V class according to MPC.