Experiment study on the remediation effects of Copper Polluted Groundwater by PRB with the volcanic as reactive medium

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Abstract: in this study, the influence s of the particle size, adsorption time, dosage, pH value and initial concentration of the solution on the removal effect of Cu (II) in groundwater were studied by batch experiments and got the static optimal reaction conditions to determine the Static influence factors firstly.

Then,based On the influence factors study, two permeable reactive barriers (PRB) with the volcanic(volcanic slag and pumice) as reactive media to remediate the Copper Polluted Groundwater were constructed and the effect and dynamics of Cu (II) removal by two groups of PRBs were discussed, the best technological conditions for removal of Cu (II) in groundwater and the remediation of Cu (II) contaminated groundwater by the volcanic slag and pumice) were confirmed and the comprehensive evaluation of the relationship between action and effect was carried out.

Finally， the regeneration methods and optimal regeneration conditions of the two volcanic rocks were explored.the experiment results were as followed :

(1) the best technological conditions for the static removal of Cu (II)including initial concentration，optimal particle size;, solid-liquid ratio , pH value, reaction time and the concussion speed, were 20mg/L, 0.15 to 0.425mm (4~100 mesh), 8g/L， 6, 2h, and 200r/min respectively.

(2) the adsorption kinetics experiments showed that the adsorption of Cu (II) by volcanic slag and pumice were much consistent with the Langmuir isothermal adsorption law, and the adsorption kinetics of Cu (II) were in accordance with the pseudo-second order kinetic model.

(3)The pumice has slightly better adsorption effect on Cu (II) than that of the volcanic slag，

(4)two permeable reactive barriers were build with volcanic slag and pumice as media to investigate the Cu (II)removal dynamic characteristics，the experiments were designed and successfully operated and both of their removal effects were very good.

(5)When the flow velocity is low (0.3mL/min), the removal rate of Cu (II) under different initial concentrations were all above 96%for the pumice PRB, the volcanic slag PRB can also achieve more than 92% removal rate for the Cu (II). but,When the flow rate rises to 0.5mL/min and 1.0mL/min,both of their removal rates decrease obviously with the prolongation of the treatment time. Compared with the volcanic slag PRB, the removal effect of the pumice PRB to Cu (II) under the different concentration gradient is better and can adapt to the Cu (II) under the condition of higher velocity (1.0mL/min). The removal of pumice PRB is the best for the removal of 10mg/L containing Cu (II) wastewater with initial concentration. The concentration of Cu (II) in the effluent can meet the requirements of the groundwater quality standard III .

(6)The effect of the volcanic slag and pumice reactive barriers in the whole process of the experiment were very good even the reaction device run after 54d, the removal rate can still maintain by about 85%. The effluent can still meet the requirement of the groundwater standard

III,so, the volcanic slag and pumice can be used as a new type of PRB medium for Cu (II) pollution groundwater in situ remediation .

Introduction

In recent years, with the rapid development of industry and the rapid increase of human activities, the situation of heavy metal pollution in China is becoming more frequent and serious[1,2]. In particular, heavy metal waste water from Cr, Cd, Ni, Pb, Hg and Cu produced in mining, smelting, electroplating, chemical industry, leather making, paper making and electronic industries, not only caused serious pollution to the surface water, but also accumulated heavy metals in the unsaturated zone, and caused the shallow groundwater with the infiltration of rain water to to lead to more and more serious irreversible heavy metal pollution[3].

The heavy metal contaminated groundwater has the characteristics of accumulation, hard degradation, mobility and difficult to treat once and thoroughly. Therefore, it has been one of the hot issues in the field of environmental protection for a long time to develop a rapid and low cost removal technology for the remediation of heavy metal pollutants in groundwater[4,5].

In twenty-first Century, the groundwater in situ remediation permeable reactive wall (Permeable reactive barrier - PRB), which was produced in 70s and 80s twentieth Century, has achieved rapid development and extensive application. Many countries such as the United States, Canada, Europe and other countries have carried out a large number of experiments and engineering applications and began more and more. At present, PRB technology has become the mainstream technology for the remediation of heavy metal polluted water in foreign countries, and the study of the selection and performance of the PRB reaction medium and the effect of pollutant removal is becoming an important research direction.

In this paper, the common volcanic rocks (crater and pumice) were used as the PRB reaction medium to construct the PRB reaction column, and the performance and influence factors of the two remediation of copper ion contaminated groundwater were studied. The kinetics of the removal of pollutants and the method of improving the adsorption performance were analyzed. In situ remediation of contaminated groundwater and comprehensive utilization of volcanic rocks can provide some technical references.

Materials and Methods

Materials

(1)the volcanic slag and pumice and pumice were purchased from a volcanic rock processing plant in Fusong County of Jilin province. The volcanic rocks and pumice were broken and sieved before the experiment. Then the deionized water was used to soak and wash the slag and pumice, and the impurities and dust were washed away. After washing, the cinder and pumice are naturally dried and placed at 105 degrees Celsius for drying 12h.

Table1 Chemical composition of scoria and pumice

	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	Na_2O	MgO	TiO_2	Others
Slag	47.7	21.3	8.9	12.4	0.5	3.0	3.4	1.7	1.2
Pumice	68.8	8.7	4.9	1.8	5.5	4.1	0.2	0.3	5.7

(2)the simulated copper waste level is called 0.393g cupric sulfate (CuSO4. 5H2O), dissolved in deionized water, moved to the bottle of 1000mL capacity, and was shaken up and kept in reserve. The concentration of the standard reserve solution is 100mg/L, which is diluted to the required concentration step by step according to the experimental requirements.

(3)reagent and instrument hydrochloric acid, nitric acid, sulfuric acid, hydroxylamine hydrochloride, sodium citrate, acetic acid, sodium acetate, 2,9- two methyl -1,10- phenanthroline, etc. (all are analytically pure); X ray fluorescence spectrometer (EAGLEIII, EDEX Co., Ltd.), 0.45 m filter membrane, 4~100 target sieves, laboratory universal grinder (DFY200C, Shanghai Yu Ming Instrument Co., Ltd.), dryer, electronic balance (BT125D, Shanghai Liangping instrument and Instrument Co., Ltd.), constant temperature concussion incubator (SKY-200B, Shanghai Su Kun Industrial Co., Ltd.), digital display pH meter (pHS-3C, Shanghai lightning Instrument Co., Ltd.), box type muffle furnace (SXL-1200M, Shanghai giant crystal precision instrument) Ltd., desktop centrifuge (TDL-40B, Shanghai Anting scientific instrument factory), multi parameter water quality analyzer (MULTP-8, Shen zhen Chang hong Technology Co., Ltd.)

Methods :

static adsorption experiment

The effects of particle size, concussion velocity, pH value, dosage of medium, concussion time on the removal of Cu (II) in the reaction medium were determined through laboratory batch experiments to obtain the optimal dynamic experimental conditions.

1)the effect of particle size on the removal of Cu (II)

The adsorbents of a certain particle size (0 ~ 0.15mm, 0.15 to 0.425mm, 0.425 to 0.85mm, 0.85 to 1.0mm, 1 to 2.0mm, 2 to 4.75mm) were respectively placed in the 250mL conical bottle and added to the Cu (II) wastewater with the 100mL concentration of 20mg/L. The fresh-keeping membrane was sealed in a constant temperature shock incubator at 20 C and 200r/min for 2h. The water samples after reaction were filtered with 0.45 m filter membrane, and the content of Cu (II) was determined, and the corresponding removal rate was calculated. Each treatment sets 3 parallel samples.

2) the effect of pH value on the removal of Cu (II)

In order to investigate the effect of pH on the removal efficiency of Cu (II), the Cu (II) solution with 100mL concentration is 20mg/L, and the pH of 0.2mol/L's HCl and NaOH to adjust the solution was 2, 3, 4, 5, 6 and 7 respectively. Then, the adsorbents of 0.15 ~ 0.425mm were respectively invoking in the tapered bottle. The fresh-keeping membrane was sealed in a constant temperature shock incubator under 20 ℃ and 200r/min for 2h. The water samples after reaction were filtered with 0.45 um filter membrane, and the content of Cu (II) was determined, and the corresponding removal rate was calculated，3 parallel samples were set in each experiment process

3)the effect of the dosage of medium on the removal of Cu (II)

The Cu (II) solution with the concentration of 100mL is 20mg/L. The pH of the solution is 6 with the HCl and NaOH of 0.2mol/L. The fresh-keeping membrane was sealed in a constant temperature shock incubator at 20 ℃ and 200r/min for 2h. The water samples after reaction were filtered with 0.45 m filter membrane, and the content of Cu (II) was determined, and the corresponding removal rate was calculated. 3 parallel samples are set in each process

4) effect of concussion time on Cu (II) removal and adsorption kinetics

The Cu (II) solution with the concentration of 100mL was 20mg/L, and pH value was 6. The adsorbent 0.8g is added to the conical bottle of 250mL, and the preservative film is sealed at the incubator of constant temperature concussion in the incubator under 20℃， 200r/min. The water samples after reaction were filtered with 0.45um filter membrane, and the content of Cu (II) was determined, and the corresponding removal rate was calculated. 3 parallel samples were set in each process In order to further study the adsorption process of Cu (II) by cinder and pumice, the pseudo second stage kinetic equation was used to fit it.

5)effect of initial concentration of solution on removal efficiency of Cu (II) and adsorption isotherms

The Cu (II) solution of the concentration of 2mg/L, 5mg/L, 10mg/L, 15mg/L, 20mg/L, 25mg/L, 30mg/L and 40mg/L is 100mL in the tapered bottle, which is adjusted to be 6, and the adsorbent is added. In the incubator with constant temperature and concussion at 20 degrees centigrade, 2h was concussion under the condition of 200r/min. The water sample after reaction was filtered with 0.45 m filter membrane, and the content of Cu (II) was measured and the corresponding removal rate was calculated. In order to further study the adsorption characteristics of Cu (II) to Cu (II) by volcanic slag and pumice, the adsorption process was fitted by Langmuir isothermal equation and Freundlich isothermal equation.

results and analysis

1) the effect of particle size on the removal of Cu (II)

The effect of particle size on the removal of Cu (II) is shown in figure 1.

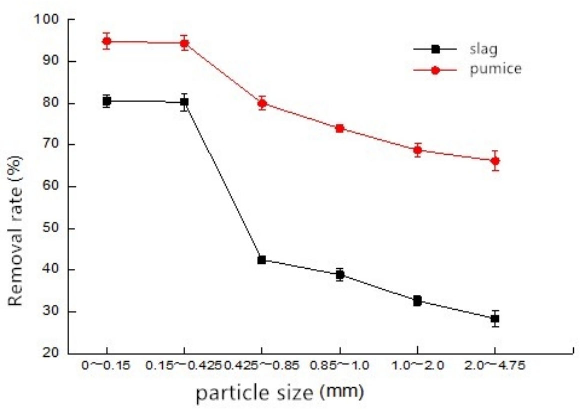


Fig. 1, removal rate of Cu (II) under different particle size

As can be seen that, when the is 2 to 4.75mm, the removal rate of Cu (II) is only 28.4% and 66.2%, respectively. With the decrease of the slag and pumice particle size, the removal rate of Cu (II) in the solution increases gradually, mainly by changing the particle size of the slag and pumice as the change of the surface of the unit mass and the surface of the pumice. The smaller the particle size, the larger the surface area of the unit mass adsorbent and the stronger the adsorption capacity for Cu (II). On the other hand, the particle size decreases, which makes the active sites available on the surface of the slag and pumice increases, and increases the amount of Cu (II) adsorbed by the cinder and pumice by chemical adsorption. When the particle size is 0.15 to 0.425mm, the removal rate of Cu (II) is 80.31% and 94.4%, respectively. The removal rate of Cu (II) by crater and pumice is 80.55% and 94.89%, respectively. The effect of particle size on removal rate is less than that of Cu (II). Under this condition, the optimal particle size of the slag and pumice bothwere 0.15 ~ 0.425mm.

2) the effect of pH on the removal of Cu (II)

The effect of pH on the removal of Cu (II) is shown in Figure 2.

As can be seen from Figure 2, the effect of pH on the adsorption of volcanic slag and pumice is more significant. The removal rate of Cu (II) by volcanic slag and pumice increases first and then increases with the increase of pH, and the overall removal rate of Cu (II) to the pumice is higher than that of the volcanic slag. PH can change the morphology of metal ions and the charge of active sites of adsorbent to affect the adsorption effect. In the range of pH 2~5, the removal rate of Cu (II) from the cinder increased from 16% to 48.9%, and the removal rate of Cu (II) from pumice increased from 28% to 78.6%. When pH<5, the morphology of Cu (II) in aqueous solution is dominated by Cu2+, and the low removal rate of Cu (II) by adsorbents may be the competitive adsorption of H+ and Cu2+ on the surface of the adsorbent because the higher mobility of H+ and Cu2+. The same charges repel each other, reducing the attraction of adsorbents to metal cations. Another reason may be that many complexation and ion exchange sites on the surface of H+ adsorbents have stronger affinity, which hinders the binding sites of metal ions close to adsorbents. When pH was 5~6, the removal rate of Cu (II) was significantly increased by the slag and pumice, which was due to the decrease of H+ concentration and activity and the decrease of the adsorption competitiveness, which was beneficial to the combination of Cu (II) ions with the adsorption site. When pH>6, the growth rate of Cu (II) removal rate in the water is slowed down, accompanied by precipitation, and the Cu (II) in the water is mainly [63] in the form of Cu (OH) 2 precipitation. It will cause blockage of PRB wall and affect its long-term operation effect, so the best pH value selected in this experiment is 6.

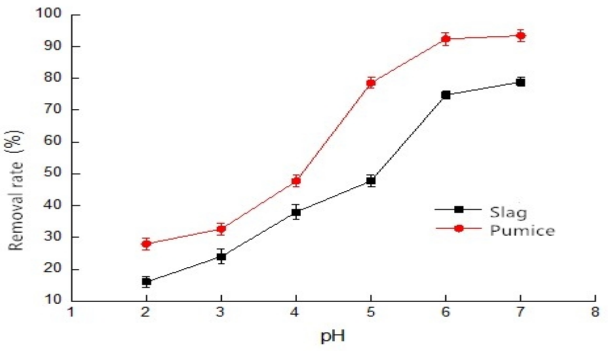


Fig.2 effect of pH value on the removal of Cu (II)

3)the effect of the dosage of medium on the removal of Cu (II)

The effect of volcanic slag and pumice dosage on the removal rate of Cu (II) was shown in Figure 3.

From the figure 3,it can be seen that the removal rate of Cu (II) increases with the increase of the adsorbent dosage . When the dosage of slag and pumice is 0.8g/100mL, with the ratio of solid to liquid is 0.4:50, the maximum removal rate of Cu (II) is reached, and the maximum removal rate is 79.6% and 96.3%, respectively. After that, the amount of slag and pumice increased, and the removal rate of Cu (II) tended to be stable. The reason that the removal rate increases with the increase of dosage may be due to the increase of the amount of adsorbents, the increase of the active sites on the surface of the adsorbent, and the increase of the removal rate. When the amount of adsorbents is reached to a certain value, the amount of adsorbent alone will not have a great

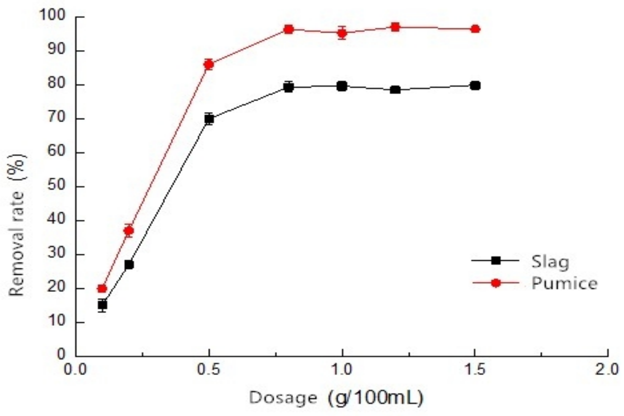


Fig.3The effect of Cu (II) removal by the dosage of medium

effect on the removal of Cu (II).

4) effect of concussion time on Cu (II) removal and adsorption kinetics

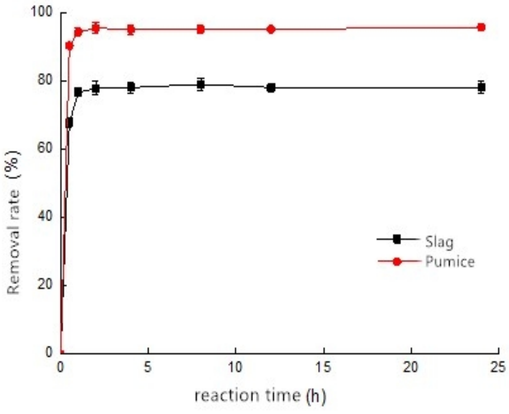


Fig4 Effect of contact time on adsorption volcanic rock

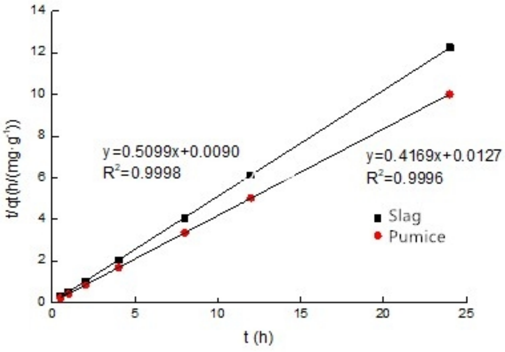


Fig5 Pseudo second-order model for Cu(II) sorption on

5) effect of initial concentration of solution on removal efficiency of Cu (II) and adsorption isotherms

The effect of initial concentration of solution on the removal of Cu (II) from cinder and pumice is shown in Figure 6，

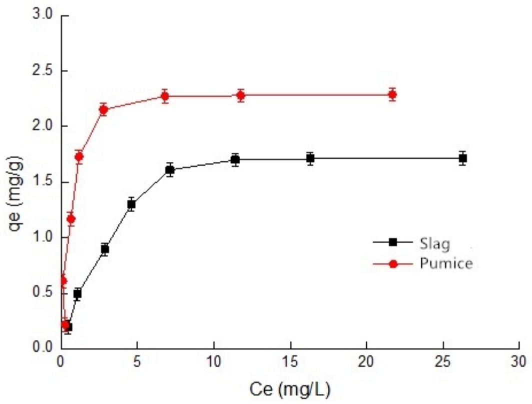
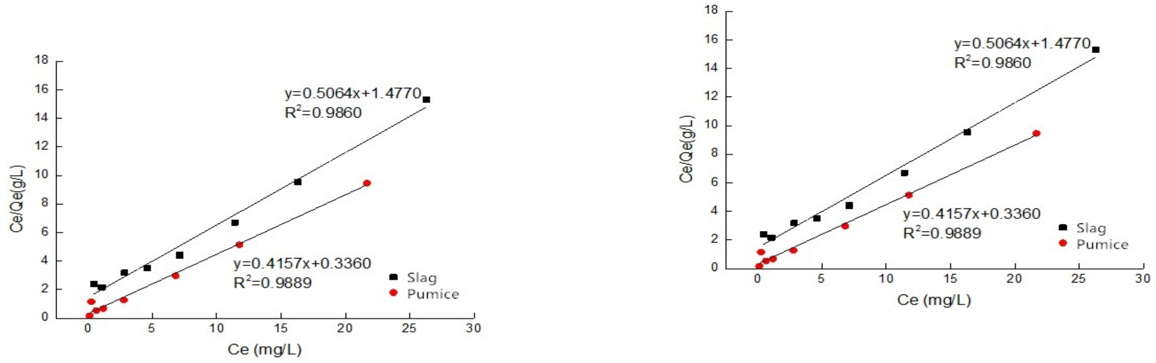


Fig.6 .Adsorption isotherms for Cu(II) on the adsorbents

from the overall trend, the adsorption capacity of two adsorbents on Cu (II) increased with the increase of initial Cu (II) concentration, and remained stable after exceeding 20mg/L. The saturated adsorption capacity of slag and pumice to Cu (II) were 1.72mg/g and 2.29mg/g respectively. It showed that the pumice has the much better adsorption capacity than the volcanic slag. But,When the concentration of Cu (II) increased from 20mg/L to 40mg/L, the removal rate of Cu (II) from the cinder decreased from 64.4% to 34.2%. The removal rate of Cu (II) by the pumice was reduced from 87.2% to 45.8%. It can be seen that the initial concentration of Cu (II) is an important parameter affecting the adsorption performance and utilization rate of the two adsorbents. It may be due to the increase of the concentration of Cu (II) ions[6,7], the binding sites are gradually occupied, and the removal rate of Cu (II) ions decreases. It can be seen that cinder and pumice have good removal effect on low concentration of Cu (II).

At the same time， the isotherm of Cu (II) adsorbed by volcanic slag and pumice were studied. The adsorption isotherms and of two adsorbents on Cu (II) and were shown in Figure

7((a)Langmuir; (b)Freundlich).



(a) (b)

Fig.7 Isotherms of Cu(II) adsorption by volcanic and pumice: (a) Langmuir; (b) Freundlich

The adsorption amount was first increased and then gradually stabilized. When the amount of adsorption capacity increased to the maximum one, it was No longer growing. With the increase of equilibrium concentration, the equilibrium adsorption capacity of pumice was much better than that of the volcanic slag indicating that pumice has a better removal effect on Cu (II) than the volcanic slag.

The Langmuir equation and Freundlich equation were selected to fit the adsorption process. . The relevant parameters of the equation were shown in Table 2. The results show that the Langmuir equation has better fitting effect on the adsorption of Cu (II) by volcanic slag and pumice, and the correlation coefficient R^2 were 0.9860 and 0.9889 respectively. The adsorption of Cu (II) by volcanic slag and pumice were1.71 and 2.28mg/g, respectively. Pumice has much higher adsorption capacity than that of the volcanic slag, which indicating that pumice was more adsorptive than the volcanic slag

Table 2 Summary of the calculated Langmuir and Freundlich isotherm constants for the Cu(II) sorption onto scoria and pumice

Adsorbents	Freundlich			Langmuir		
	K_f	1/n	R^2	Ka(L/mg)	q_m(mg/g)	R^2
Slag	0.691	0.5417	0.8665	0.3428	1.975	0.9860
Pumice	1.101	0.3647	0.5982	1.237	2.406	0.9889

conclusions

1) the best technological conditions for the static removal of Cu (II) are the initial concentration of 20mg/L, the particle size of 0.15 to 0.425mm (4~100 orders), the solid-liquid ratio 8g/L, the pH value 6, the reaction time 2h, the concussion speed 200r/min

2) the adsorption kinetics showed that the adsorption of Cu (II) by volcanic slag and pumice was more consistent with the Langmuir isothermal adsorption law, and the adsorption kinetics of Cu (II) were in accordance with the quasi two order kinetic model.

3)the adsorption effect of pumice on Cu (II) is slightly better than that of volcanic slag, and Cu (the experimental results of dynamic column removal by II removal) is carried out by using both as filling medium to construct the permeable reaction wall.

When the flow velocity is low (0.3mL/min), the removal rate of Cu (II) with different initial concentration is above 96%, and the removal rate of Cu (II) can be achieved by the craterreactivebarrier to Cu (II). When the flow rate rises to 0.5mL/min and 1.0mL/min, the removal rate of each reaction column decreases obviously with the prolongation of the treatment time. Compared with the crater reaction wall, the removal effect of the pumice reactive barrier to Cu (II) under the different concentration gradient is better and can be more adapted to the removal of Cu (II) under the condition of high velocity (1.0mL/min). The removal effect of pumice PRB and crater PRB is best for the initial concentration of 10mg/L containing Cu (II) wastewater. The concentration of Cu (II) in the effluent can meet the requirements of the standard of the third grade standard of groundwater quality.

4)the effect of the volcanic rock reactive barrier in the whole process of the experiment is good. the removal rate can still be maintained at about 85% even after the device runs 54d,the effluent can still meet the standard of groundwater quality III, so the pumice and the slag can be used as a new type of PRB medium to remediate the Cu (II) polluted groundwater.

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