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ANION EXCHANGE RESIN-SUPPORTED nZVI PERMEABLE REACTIVE BARRIERS FOR REMOVAL OF NITRATES FROM GROUNDWATER

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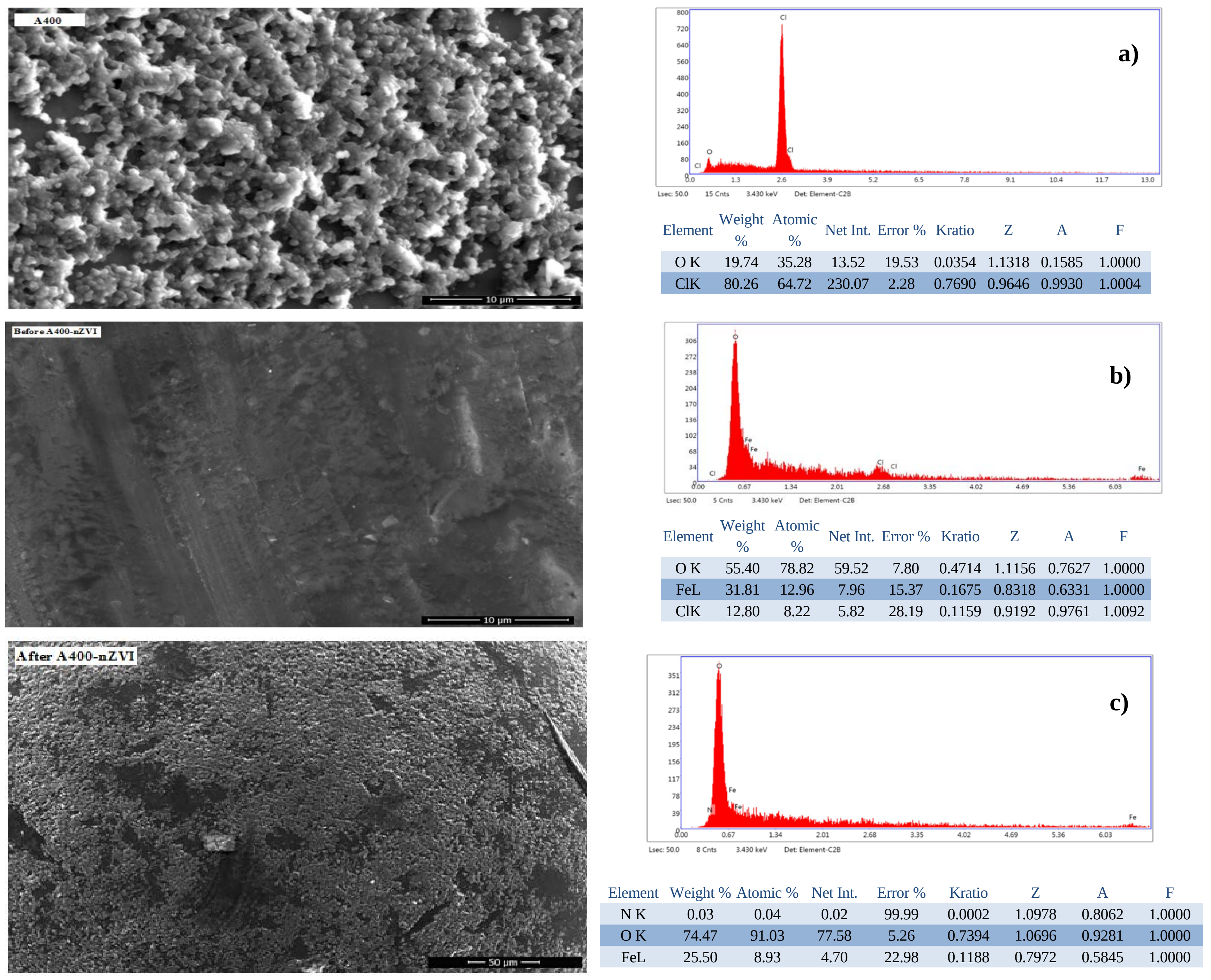
Abstract

The use of zero-valent iron nanoparticles (nZVI) as a reactive medium in permeable reactive barriers (PRBs) has often been used to remediate contaminated groundwater especially with oxo-anions such as nitrates and chromates, as well as chlorinated organics. Nitrates have received special attention because they can easily reach groundwater, the main source being agricultural activities. However, ZVI nanoparticles have some limitations in practical applications. The main drawback is that they are extremely small in size and can easily agglomerate due to their colloidal and magnetic characteristics. To solve the issue regarding the nZVI tendency to get agglomerated when used alone, a wide range of supporting materials were used to immobilize nZVI without decreasing its reactivity. In this respect, both organic materials (i.e. ion exchange resins, chelating resins, polymeric substrates, etc.), as well as inorganic materials (i.e. clay minerals, metal oxides, zeolites, etc.) were used. The physico-chemical characteristics of the materials used as support have a major influence on the size and distribution of nZVI particles immobilized on them. Also, the support material has the role of concentrating the reactive phases by adsorption, which favors the redox reactions that take place in the system. Therefore, this paper tests the performance of a new reactive barrier, based on nZVI deposited on a strongly basic anion exchange resin for removing nitrates from a simulated groundwater.

Materials and Methods

Zero-valent iron nanoparticles (nZVI) were obtained by the reduction reaction of ferrous ions with sodium borohydride ($NaBH_4$) at the surface of a strong base anion exchange resin (Purolite A400). Thus, a solution of ferrous sulfate was prepared and contacted with the ion exchange resin at various solid-liquid mass ratios. Sodium borohydride was then added dropwise with continuous stirring under an oxygen-free atmosphere. The black solid particles formed were first separated by filtration, rinsed several times with ethanol, dried and kept in an oxygen-free atmosphere until use. The new permeable reactive barrier (nZVI-Purolite A400) was tested for the removal of nitrates from a simulated groundwater under various working conditions. The composition of the simulated groundwater was set as 30 mg/L SO_4^{2-}, 140 mg/L Na^+, 30 mg/L Cl^-, 100 mg/L HCO_3^-, 80 mg/L Ca^{2+}, and 50 mg/L K^+. Therefore, the simulated groundwater containing 10, 40, and 100 mg/L NO_3^-, were mixed under continuous stirring with the reactive barrier at a liquid-to-solid mass ratios of 5 for a contact time of 2 to 60 minutes. The experiments were carried out at a simulated groundwater pH of 3 and 8.

Characterization of A400-nZVI



Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	19.74	35.28	13.52	19.53	0.0354	1.1318	0.1585	1.0000
ClK	80.26	64.72	230.07	2.28	0.7690	0.9646	0.9930	1.0004

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
O K	55.40	78.82	59.52	7.80	0.4714	1.1156	0.7627	1.0000
FeL	31.81	12.96	7.96	15.37	0.1675	0.8318	0.6331	1.0000
ClK	12.80	8.22	5.82	28.19	0.1159	0.9192	0.9761	1.0092

Element	Weight %	Atomic %	Net Int.	Error %	Kratio	Z	A	F
N K	0.03	0.04	0.02	99.99	0.0002	1.0978	0.8062	1.0000
O K	74.47	91.03	77.58	5.26	0.7394	1.0696	0.9281	1.0000
FeL	25.50	8.93	4.70	22.98	0.1188	0.7972	0.5845	1.0000

Figure 1. SEM images for (a) original resin, (b) A400-nZVI before reaction N, (c) A400-nZVI after reaction

Results

The relevant parameters obtained using the pseudo first order and pseudo second order models are shown in Table 1.

Table 1. Kinetics parameters for A400-nZVI

A400-nZVI							
pH	***C (mg/L)***	***Pseudo first order***		***Pseudo second order***			
		k'	R^2	k''	v_0 *(mg/g·min)*	a_{eq} *(mg/g)*	R^2
3	10	0.0585	0.7099	0.7201	0.6902	0.9790	0.9988
	40	0.0601	0.7131	0.330	5.1443	3.9479	0.9999
	100	0.058	0.7409	0.1019	9.7601	9.7859	0.9999
8	10	0.0413	0.9191	0.2167	0.1805	0.9126	0.9940
	40	0.0506	0.8588	0.1268	1.8603	3.8295	0.9995
	100	0.0521	0.8161	0.0572	4.8823	9.2412	0.9997
A400-nZVI (aquifer)							
pH	***C (mg/L)***	***Pseudo first order***		***Pseudo second order***			
		k'	R^2	k''	v_0 *(mg/g·min)*	a_{eq} *(mg/g)*	R^2
3	10	0.059	0.8033	0.9567	0.6385	0.8171	0.9996
	40	0.0512	0.7889	0.2503	3.0542	3.4934	0.9979
	100	0.0526	0.8051	0.1163	7.878	8.230	0.9990
8	10	0.0555	0.7895	1.6023	0.3845	0.4898	0.9999
	40	0.0477	0.7877	0.2660	1.6934	2.5231	0.9973
	100	0.0462	0.8292	0.0747	3.8014	7.129	0.9967

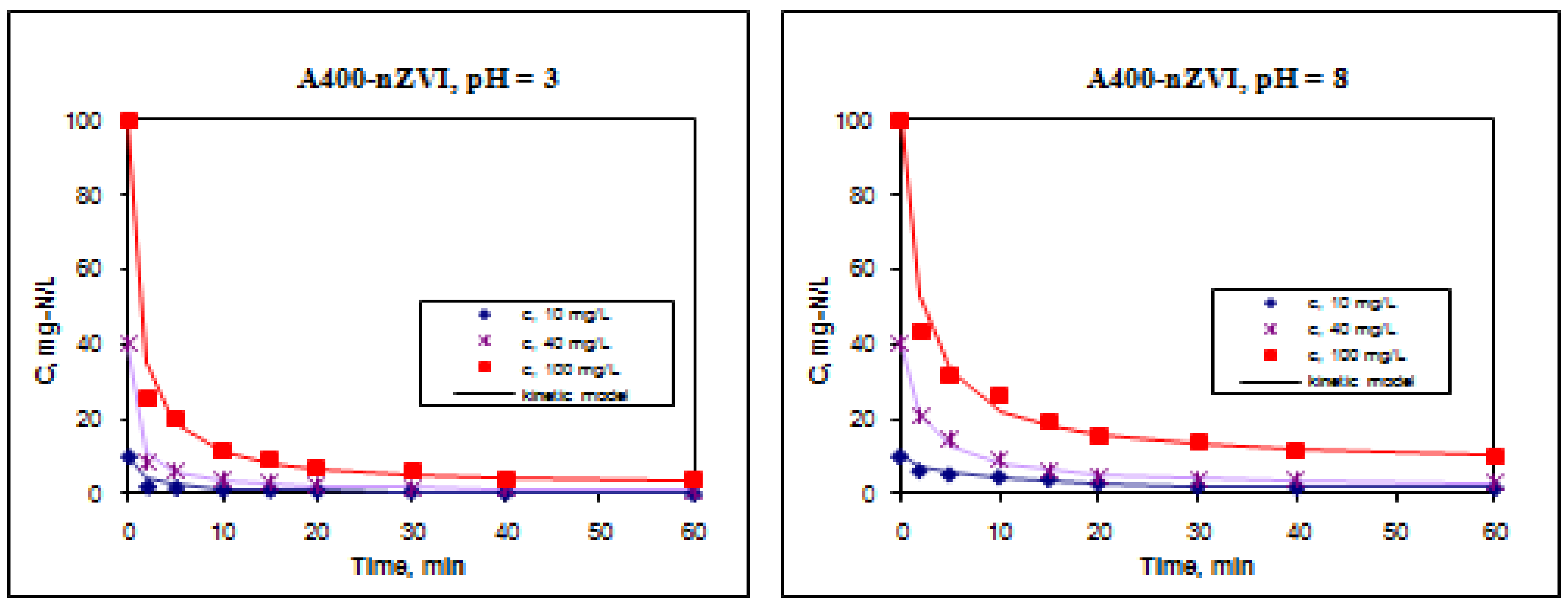


Figure 2. Variation of concentration in time for A400-nZVI at pH= 3 and 8

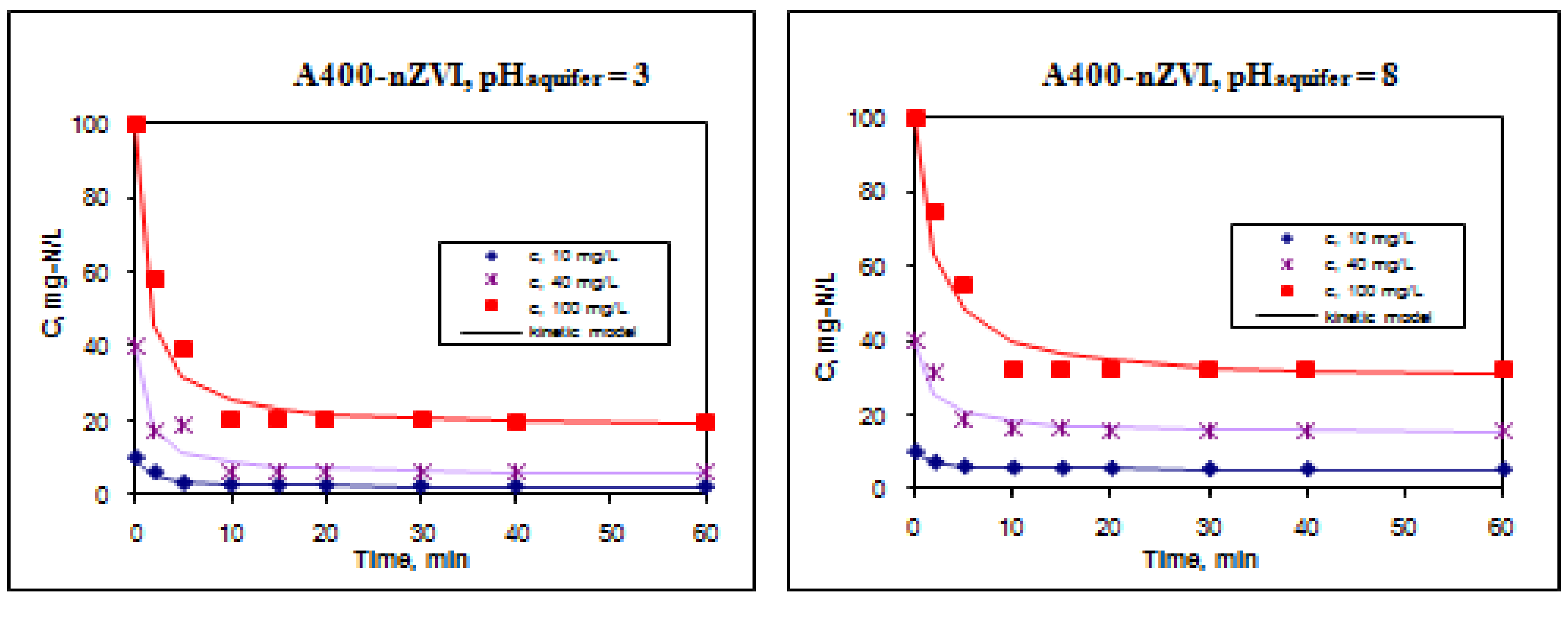


Figure 3. Variation of concentration in time for A400-nZVI at pH= 3 and 8 in simulated groundwater

Conclusion

The much better result of nitrate removal efficiency obtained in acidic conditions can be explained by the fact that the protons introduced into the system not only favor the reduction of nitrates, but also inhibit the formation of iron oxides. Also, a large part of ferrous ions are formed in the system by the reduction of these protons by zero-valent iron, which subsequently favor the reduction of nitrates. The experimental results revealed that Purolite A400-nZVI has a high efficiency for the removal of nitrates from aqueous solutions especially under acidic conditions. In this respect, it was found that over 80% of the nitrate is removed at a pH values of initial nitrate solution ranging from 3 to 8, corresponding to an initial concentration of nitrate in the initial solution ranging from 10 to 100 mg/L.

Acknowledgements

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