Methylene blue removal from contaminated waters using O_3, natural zeolite, and O_3/zeolite

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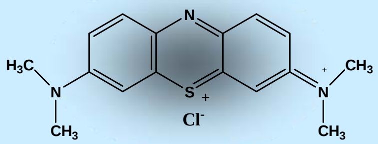
INTRODUCTION

Molecular structure of methylene blue

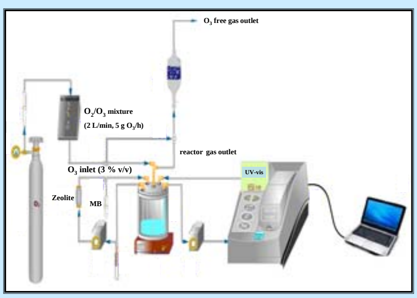


OBJECTIVES

This work compares experimental results on methylene blue (MB) removal systems based on ozone oxidation (O_3), zeolite adsorption (Zeolite), and simultaneous adsorption-oxidation using ozone in the presence of natural zeolite (O_3/Zeolite).

METHODS

Experimental system



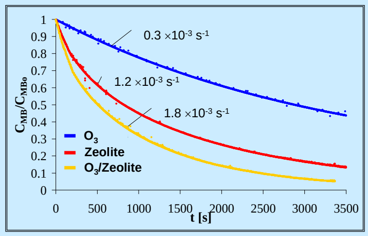
Physicochemical characterisation of natural zeolite

Physical characteristics	Specific gravity (g/cm^3)	2.2
	S_{N2} (m^2/g)	205
	V_p (cm^3/g)	0.12
Mineralogical composition	Clinoptilolite (%)	53
	Mordenite (%)	40
	Quartz (%)	7
Chemical characteristics	SiO_2 (%)	67
	Al_2O_3 (%)	13
	TiO_2 (%)	0.2
	Fe_2O_3 (%)	2
	Na_2O (%)	2.6
	K_2O (%)	0.45
	CaO (%)	3.2
	MgO (%)	0.69
	CEC (meq/g)	2.05
	pH_{PZC}	7.9
	Acid sites (μeq/g)	220
	Basic sites (μeq/g)	960

RESULTS AND DISCUSSION

1.- COMPARISON OF MB REMOVAL USING O_3, Zeolite, O_3 /Zeolite

T= 20 °C, pH = 2, 15 g/L Zeolite, C_{MBo}= 30 mg/L, C_{O3o}= 6 mg/L.



2.- EFFECT OF pH ON MB REMOVAL RATE

T= 20 °C, pH (2-8), 15 g/L Zeolite,

C_{MBo}= 30 mg/L, C_{O3o}= 6 mg/L.

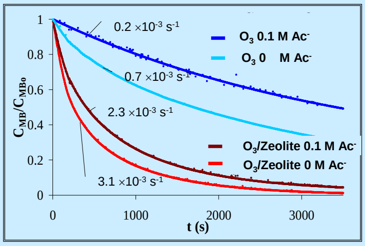
Process	Apparent first order rate constant × 10^{-3} (s^{-1})		
	pH 2	pH 6	pH 8
O_3	0.3	0.5	0.7
Zeolite	1.2	1.2	1.2
O_3/Zeolite	1.8	2.6	3.1

The O_3/zeolite treatment enhanced MB removal for each pH level studied. This could be related to different reactivity of ozone toward metal oxides sites of the zeolite surface, which exhibit pH-dependent charges.

3.- EFFECT OF THE PRESENCE OF RADICAL SCAVENGERS

T= 20 °C, pH= 8, 15 g/L Zeolite,

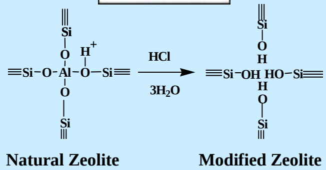
C_{MBo}= 30 mg/L, C_{O3o}= 6 mg/L



The reduction on on MB removal rate by acetate ions could be related with the inhibition of radical chain reactions taking place in the bulk solution. In the combined O_3/zeolite process, the oxidation reactions of MB mainly occur on zeolite surface.

3.- EFFECT OF ZEOLITE CHEMICAL SURFACE CHARACTERISTICS ON MB REMOVAL RATE

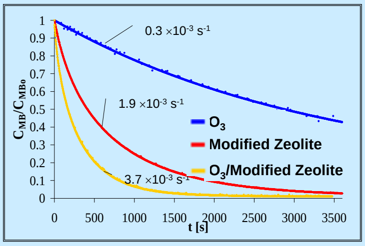
Zeolite chemical modification by refluxing in HCl



Natural Zeolite		Modified Zeolite
205	S_{N2} (m^2/g)	344
0.09	V_{micro} (cm^3/g)	0.16
0.03	V_{meso} (cm^3/g)	0.004
220	Acid sites (μeq/g)	1240
960	Basic sites (μeq/g)	70
7.8	pH_{PZC}	2.7
21.8	X_m (mg/g)	35.8

T= 20 °C, pH = 2, 15 g/L Modified Zeolite,

C_{MBo}= 30 mg/L, C_{O3o}= 6 mg/L.



CONCLUSIONS

Heterogeneous ozonation process promoted by zeolite increased MB removal rate, as compared with homogeneous ozonation and single zeolite adsorption treatments.

In the combined treatment, the effects of radical inhibitors are reduced due to the presence of zeolite, suggesting that zeolite surface plays a fundamental role in the reaction mechanism.

Zeolite provided a contact place for reactions between MB, ozone, and radicals. At $pH>pH_{PZC}$, zeolite increases the MB ozonation rate. This could be explained by the enhancement on ozone decomposition reactions with ionised strong Lewis acid surface groups on metal oxide surface sites of the zeolite.

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