BABEŞ-BOLYAI UNIVERSITY

FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING

DOCTORAL SCHOOL OF CHEMISTRY

Eng. CHICINAŞ RALUCA CORINA
(căs. **PLEŞA CHICINAŞ)**

ABSTRACT OF PhD THESIS

Scientific advisor:
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ABSTRACT OF PhD THESIS

REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATER BY NON-DESTRUCTIVE AND DESTRUCTIVE METHODS

PhD Commission:

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2018

Preface

This doctoral thesis has been developed during the course of doctoral research conducted at the Faculty of Chemistry and Chemical Engineering, University Babes-Bolyai University of Cluj-Napoca during the period October 2013 - September 2016 under the supervision of Prof. Dr. Ing. Mircea DĂRĂBANŢU, HDR. Guidance Committee consisted ofConf. Dr. Cornelia MAJDIK, Conf. Dr. Cerasella-Liliana INDOLEAN and Conf. Dr. Ing. Castelia Eugenia CRISTEA.

During the period October 2014 – Septemer 2015 author received a scholarship awarded by the Sectoral Operational Program Human Resources Development 2007-2013, financed by the European Social Fund in POSDRU / 159 / 1.5 / S / 132 400, entitled „Tineri cercetători de succes – dezvoltare profesională în context interdisciplinar şi internaţional”.

Table of Contents

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When drafting the summary were kept the same notations for chapters, paragraphs, figures, tables used in the PhD thesis.

INTRODUCTION

Water is an essential element for sustaining life on Earth and its quality is crucial for the future of humanity. Changes resulting from human activity on the water cycle and (in)direct water pollution, have a profound effect on water availability and quality.

The wastewaters are contaminated with a variety of pathogens, organic and inorganic pollutants. If they are not properly removed before release to the environment, these pollutants contribute to the emergence of public health problems and environmental pollution.

The main purpose of this PhD research work undersigned REMOVAL OF ORGANIC POLLUTANTS FROM WASTEWATERS BY NON-DESTRUCTIVE AND DESTRUCTIVE METHODS was to study the possibility of using natural materials (zeolitic volcanic tuff, diatomite and bentonite) and carbon xerogel in catalytic wet air oxidation of organic compounds from watewaters.

Relevance of the research is supported by the finding that, currently, the volumes of wastewaters increasingly fast which requires finding cheap and effective treatment methods Thus, there have been proposed two lines of research (i) organic dyes removal from wastewater by adsorption and (ii) phenol removal from wastewater by catalytic wet air oxidation.

PhD Thesis is structured:

- **Bibliographic study** – Chapter I
- **Original contributions** – Chapter II and III which presents experimental results.

Chapter I - related general aspects of existing of organic pollutants in the environment, non-destrutive methods (adsorption and ionic exchange), destructive (catalytic wet air oxidation) to eliminate, by treating wastewaters. Are described the theory aspects of the techniqs used for structural characterization of materials used in the study subject of this work**.**

In **Chapter II** are presented, investigation methods and organic dyes adsorption experimental results, from wastewater, using zeoltic volcanic tuff, diatomite, bentonite and carbon xerogel as adsorbents.

Chapter III describe phenol CWAO experimental results using metals modified zeolitic volcanic tuff, metals modified diatomite and metals doped carbon xerogel as catalysts.

The end of the work includes references and scientific activity.

Doctoral Research strategy consisting of the following objectives:

- *Adsorbents* preparation:

- zeolitic volcanic tuff
- diatomite
- bentonite
- carbon xerogel

- *Catalysts* preparation:

- zeolitic volcanic tuff
- diatomite
- carbon xerogel

- Adsorbents and catalysts *structural characterization* by: S_{BET} – specific surface, *Brunauer, Emmett, Teller* method, SEM-EDX (*Scanning Electron Microscopy - Energy Dispersive X-ray Spectroscopy*), TEM (*Transmission Electron Microscopy*), XRD (*X-ray diffraction*) şi FTIR (*Fourier Transform Infrared Spectrometry*).
- Determination of the *performance* of adsorbents in the removal process of organic dyes from aqueous solution by investigating the optimum conditions of temperature, concentration of pollutants, adsorbent particle size and quantity.
- Determination of the *performance* of catalysts in the removal process of phenol from aqueous solution by investigating the optimum conditions of temperature, concentration of pollutants, air flow and quantity.
- *Kinetics and thermodinamic parameters* of organic dyes adsorption process
- *Kinetics and thermodinamic parameters* of phenol CWAO process.

The results were used for the publication of 6 articles in ISI (*Separation and Purification Technology, Journal of Molecular Structure, Environmental Science and Pollution Research, Analytical Letters* şi *Studia UBB Chemia*) and 7 internaţional conferences.

Keywords: diatomite, bentonite, zeolitic volcanic tuff, carbon xerogel, adsorbant, catalyst, adsorption, catalitic wet air oxidation, phenol, dyes, kinetics, adsorption isotherms, thermodynamics, reaction mechanism.

CHAPTER II. ORIGINAL CONTRIBUTIONS.

STUDIES ON ORGANIC DYES REMOVAL, FROM AQUEOUS SOLUTION, USING NONDESTRUCTIVE METHODS: ADSORPTION

1. "*Ability of a montmorillonitic clay to interact with cationic and anionic dyes in aqueous solutions*"
Raluca Pleşa Chicinaş¸ Horea Bedelean, Răzvan Ştefan, Andrada Măicăneanu
Journal of Molecular Structure, **2018**; 1154: 187–195.

2. "*Romanian (Măcicaş) zeolitic volcanic tuff for malachite green removal*"
Raluca Pleşa Chicinaş, Horea Bedelean, Andrada Măicăneanu
Studia UBB Chemia, LXI, **2016**; 4: 243-254.

3. "*Characterization of Romanian bentonitic clays for the removal of dyes from wastewater*"
Raluca Pleşa Chicinaş, Adriana Tănase, Horea Bedelean, Andrada Măicăneanu
Analytical Letters, **2016**; 49: 2686-2701.

ABSTRACT

In this chapter are presented organic dyes Toluidin Blue, Malachite Green and Congo Red adsorption process results, using zeolitic volcanic tuff, diatomite, bentonite and carbon xerogel adsorbents. Structural characterizations was studied using SEM-EDX, TEM, XRD şi FTIR. Suprafaţa specifică, S_{BET} (BET method) techniques. Adsorption experiments were realised in batch. *Langmuir*, *Freundlich*, *Temkin* and *Dubinin-Radushkevich* adsorption isotherms were applied. Kinetics and thermodynamic parameters were also studied.

Keywords: adsorption, organic dyes, adsorption isotherms, kinetics and thermodinamics

II.1. MATERIALS AN METHODS

II.1.1. Natural adsorbents

II.1.1.1. *Zeolitic volcanic tuff*

A representative sample of zeolitic volcanic tuff (ZVT) collected from Măcicaş deposit (Cluj County, Transylvania, Romania) was used. The high quantity of secondary and hydrated material is indicated by the high value of loss of ignition (12.00%). The samples under investigation showed a remarkable homogeneity in their mineralogical and chemical composition with a small variation in SiO_2 content. Also, the ZVT is low in Na and K content, but high in Ca. The main component of the ZVT is represented by volcanic glass (70-80%) as fragments with angular edges, pyrogenic materials also include K-feldspars, plagioclases, quartz, micas, amphiboles and opaque minerals. ZVT X-ray diffraction patterns obtained indicated the massive presence of clinoptilolite as the main zeolite species. The semi-quantitative estimation from XRD patterns indicated that the zeolite content reached values up to 80% from the crystallized fractions of the tuff. The ZVT contains abundant tabular clinoptilolite crystals that formed by the replacement of the vitric fragments. Finally, FTIR spectra of the ZVT samples indicated the presence of specific zeolite peaks.

II.1.1.2. *Diatomite* (**D**)

Diatomite sample (raw diatomite) collected from Minișul de Sus deposit, Arad County, Romania was used as adsorbent in this study. Characterization of diatomite samples was realized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (EDX) and Fourier Transformed Infrared Spectroscopy (FTIR).

II.1.1.3. *Bentonite* (**B**)

Four bulk samples extracted from the bentonite deposits of Oraşul Nou (Satu Mare County), Petreşti (Cluj County), Valea Chioarului (Maramureş County) and Gurasada (Hunedoara County) deposits, Transylvania, Romania, were used as adsorbents for dyes removal from wastewaters. Compositional characterization of the bentonites was realized using X-ray diffraction (XRD), scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS), specific surface area (SSA) using Brunauer-Emmett-Teller method (BET) and Fourier transformed infrared spectroscopy (FTIR) analysis.

In Romania, bentonitic clays occur in various places, sometimes forming ore deposits (Brana, Avramescu, and Călugăru 1986). Some of the deposits are well-known and were partially mined in the past. The bentonitic clays used, were selected for being tested due to their properties and efficiencies related to a high degree of purity (Bedelean et al. 2010).

II.2. ZEOLITIC VOLCANIC TUFF USED FOR ORGANIC DYES REMOVAL FROM AQUEOUS SOLUTION

II.2.1. Zeolitic volcanic tuff preparation by pre-processing

Raw ZVT was subjected to a grinding process, followed by size separation in order to obtain the 0.2-0.4, 0.4-0.6, 0.6-1.0, 1.0-1.25 and 1.25-1.6 mm fractions, which were further used throughout the experiments. Raw ZVT was then washed few times with distilled water in order to remove fine particles and dried at 105°C for 24 h.

All reagents were of analytical purity and used as received. Distilled water was used throughout this work.

II.2.3. The results of the removal of organic dyes Toluidine Blue and Malachite Green from aqueous solutions using Zeolitic Volcanic Tuff

II.2.3.1. *Toluidin Blue*

Our study on the TB removal from aqueous solution using zeolitic volcanic tuff (TVZ) consist in investigation of the influence of following parameters:

a) **TB** *initial concentration*

In Figure 6 is presented TB initial concentration time evolution.

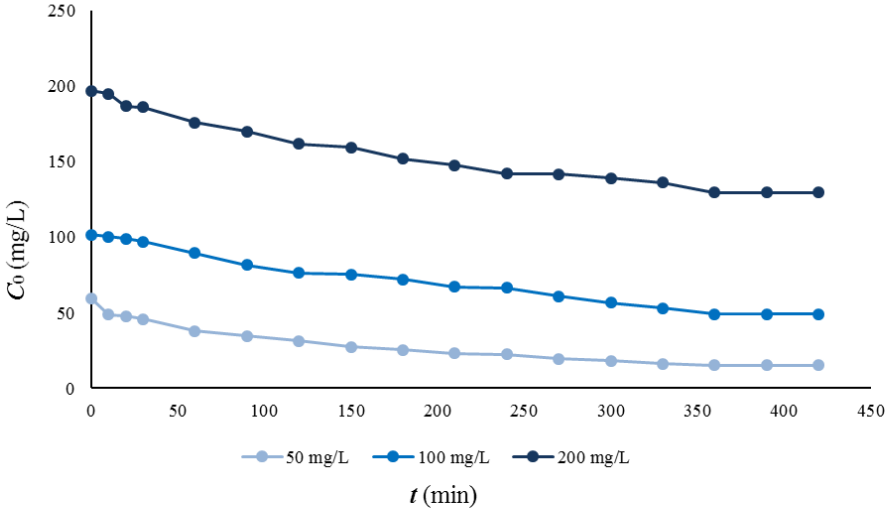


Figure 6. TB initial concentration time evolution (C_0)
(T = 25 °C; 0.50 g **TVZ**: 10 mL soluţie **TB**; d_{TVZ} = 0.60-1.00 mm; t = 420 min)

Adsorption - desorption thermodynamic equilibrium was reached after approx. 360 minutes in all three cases. Increasing of dye initial concentration was parallel to the increase in the adsorption capacity of TVZ, which demonstrates a high retention capacity even at high concentrations. The maximum TB removal efficiency of 81% was obtained when the initial concentration of the solution was 50 mg / L.

b) *Adsorbent quantity*

The influence of solid (g TVZ) : liquid (mL, TB) ratio on the removal efficiency of dye has been studied for the following values: 0.25: 10 0.50: 10 0.75: 10 1.00: 10 g / mL. Results showed that the maximum efficiency of removal of TB (70%) was obtained in the case of solid: liquid ratio of 0.50 g: 10 mL.

c) *Adsorbent grain size*

Increasing of TVZ grain size was accompanied by a slight increase in the adsorption capacity; thus, the maximum values of η and qe were 0.90 mg / g and 75%, obtained for the granules in 1.25-1.60 mm range.

d) *Temperature influence*

Increasing of temperature resulted in increasing the amount of dye retained, and hence the adsorption capacity of the TVZ process is therefore one endothermic. The maximum efficiency of TB removal was 52% at a temperature of 55 °C.

II.2.3.2. *Malachite Green* (**MG**)

Our study on the MG removal from aqueous solution using zeolitic volcanic tuff (TVZ) consist in investigation of the influence of following parameters:

a) **MG** *initial concentration*

The results obtained for various initial concentrations of MG solution (10-250 mg/L) are presented. An increase of MG initial concentration led to an increase in the ZVT adsorption capacity, proving that the considered material has a high ability to retain MG even at high concentrations.

b) *Asorbent quantity*

The study of the solid:liquid ratio influence upon MG adsorption process was conducted using solid:liquid ratios in 0.25:10-1.00:10 g/mL interval. Thus, an increase in adsorbent quantity led to a decrease in adsorption capacity value due to the fact that for the same initial concentration, a higher surface or adsorbent quantity is available for adsorption. The highest removal efficiency calculated in this case was about 97% for 1.00:10 mg/L.

c) *ZVT grain size*

The influence of the ZVT grain size upon the adsorption capacity in the MG adsorption process was studied for a range of grain sizes in 0.2-0.4 to 1.25-1.6 mm interval. Adsorption capacities values thus obtained for all grain sizes are presented in Figure 4. This evolution might be correlated with diffusional limitations that occur due to the MG molecule size, adsorption taking place mostly on the external surface of the grain. Removal efficiency values followed the same trend with a maximum value of about 98% for 1.25-1.60 mm.

d) *Temperature influence*

The influence of temperature on MG adsorption was investigated using the following reaction conditions: solid:liquid ratio 0.50:10 g/mL, 50 mg MG/L, 0.6-1.0 mm adsorbent grain size, and a reaction time of 360 min. The acquired results, showed that an increase of the contact time has as result a gradually increase of the MG uptake with a higher rate for temperatures between 35 and 55°C in the first 100 min and then slower towards the equilibrium. Adsorption equilibrium was reached in about 300, 240, and 120 min as the temperature increased from 25 to 55°C. Removal efficiency increases from 72 to 93% as the temperature increases from 25 to 55°C.

II.2.4. Adsorption isotherms of Toluidine Blue and Malachite Green adsorption process using Zeolitic volcanic tuff

Equilibrium experiments were carried out for different initial concentrations in 10-250 mg/L range at 25°C for 420 min.

In cese of TB, the higher value of R^2, 0.9757, was obtained in the case of Langmuir model, which describes the well-studied, suggesting the same time, TB monolayer coverage of the outer surface TVZ granules.

In order to establish which isotherm model describes better the adsorption of MG on ZVT, Langmuir, Freundlich, Dubinin-Radushkevich and Temkin equations were considered. The parameters obtained from experimental data and the related correlation coefficients are presented. All values of correlation coefficient (R^2) were higher than 0.9, but Temkin model yields a better fit, with a 0.9864 value, than Langmuir, Freundlich and Dubinin-Radushkevich models, with 0.9421, 0.9275, and 0.9490, respectively. Previous studies in similar systems showed that the adsorption of dyes (methyl orange and methyl violet) was best described by Temkin model.

II.2.5. Thermodynamic parameters of Toluidine Blue and Malachite Green adsorption process using Zeolitic volcanic tuff

The adsorption of TB and MG dye onto ZVT was studied at temperatures in 298-328 K interval. In order to estimate the effect of temperature on the for the considered adsorption system, Gibbs free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were determined. ΔH^0 positive value, also less the 84 kJ/mol indicates the endothermic nature and that the process is physical in nature. The small positive value of ΔS^0 confirmed the increased randomness at the solid-solution interface during adsorption. ΔG^0 values for all temperatures are positive, and the value decrease with increase of temperature, which indicates the fact that the considered adsorption process will be promoted by specific temperature conditions, leading to increased adsorption capacities.

II.2.6. Kinetics of Toluidine Blue and Malachite Green adsorption process using Zeolitic volcanic tuff

The rate constants and the adsorption mechanism of TB and MG adsorption onto ZVT were evaluated by using different kinetic models, such as pseudo first-, pseudo-second-order, intra-particle, and liquid film diffusion. The results obtained for all considered kinetic models are presented. Taking into consideration the correlation coefficients obtained for all considered models, the fact that $q_{e,calc}$ for pseudo-first- and pseudo-second-order exhibit considerable difference towards the $q_{e,ext}$ values, and also that the intercept values in case of diffusion models are very close to 0, support the conclusion that intra-particle diffusion might be rate-determining step for this system (concentrations higher than 50 mg/L). Experimental results obtained for various grain sizes of the ZVT (adsorption capacity increase with an increase in grain size) also support this conclusion.

The pore diffusion coefficients were determined, with the smallest value of 8.69×10^{-10} cm^2/s. Although the values are not in the rate determining range (10^{-11} - 10^{-13} cm^2/s) [13-14] it is reasonable to assume that internal diffusion plays a significant role for the considered system especially in the higher concentration rage.

II.2.7. Conclusions

Zeolitic volcanic tuff collected from Măcicaş deposit (Cluj County) has been studied as adsorbent in the TB and MG adsorption process from aqueous solution. The study of the influence of various adsorption process parameters (dye initial concentration, solid: liquid ratio, particle size of the adsorbent and the temperature) led to the establishment, in each case, the following optimal conditions for the process:

- **TB**: T = 55 °C; C_0 = 50 mg/L; 0.50 g **TVZ** : 10 mL sol. aq. **TB**; $d_{\mathbf{TVZ}}$ = 1.25-1.60 mm.
- **MG**: T =55 °C; C_0 = 250 mg/L; 1.00 g **TVZ** : 10 mL sol. aq. **MG**; $d_{\mathbf{TVZ}}$ = 1.25-1.60 mm.

In these conditions, maximum removal efficiencies were 80% (TB) and 99% (MG).

Modeling of the thermodynamic equilibrium processes revealed Langmuir isotherm valid in case of TB and Temkin in case of MG.

The thermodynamic study indicated retention processes of both dyes as physical, spontaneous and endothermic.

Kinetic Modeling has indicated the internal diffusion rate-limiting step for both dyes.

II.3. DIATOMITE USED FOR ORGANIC DYES REMOVAL FROM AQUEOUS SOLUTION

II.3.1. Preparation of treated diatomite

Diatomite sample (raw diatomite) collected from Minișul de Sus deposit, Arad County, Romania was used as adsorbent in this study. Characterization of diatomite samples was realized using X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (EDX) and Fourier Transformed Infrared Spectroscopy (FTIR).

Raw diatomite was first subjected to a grinding process, followed by size separation in order to obtain the 0.6-1.0 mm fraction, which was further used throughout the experiments. Raw diatomite was then washed few times with distilled water in order to remove fine particles and dried at 105°C for 24 h.

The following treatments were applied to the raw diatomite: thermal, chemical, thermo-chemical and ultrasonic. In case of the thermal treatment, modified after, raw diatomite was calcined at different temperatures in 250-750°C interval for 1, 2 and 4 h. Chemical treatment, was realized using HCl solution of different concentrations (1 M, 2 M and 4 M). Raw diatomite and acid solution were contacted at room temperature under stirring (300 rpm) for 3 h at a solid : liquid ratio of 1:10. The obtained samples were separated from acid solution, thoroughly washed with distilled water until no chlorine was detected ($AgNO_3$ 0.01 N) and dried at 105°C for 24 h. Thermal and chemical treatment were also combined, when raw diatomite was first treated with HCl 2M in the same conditions as described above and then calcined at different temperatures for 2 h. Ultrasonic treatment, modified after Zhang et al., was realized using each time 20 g of raw diatomite and 100 mL distilled water in a glass beaker, which was then placed in an ultrasonic bath at room temperature at different powers for various time intervals. After ultrasonic treatment, the solid was recovered by settling, washed with distilled water and dried at 105°C for 24 h.

Table 9. Diatomite types notation

Treatment	Conditions			
Thermal (T)	*T* (°C)	Timp (h)		
	250	2		$\mathbf{D}_{\mathrm{T}}$-250-2
	500	1		$\mathbf{D}_{\mathrm{T}}$-500-1
	500	2		$\mathbf{D}_{\mathrm{T}}$-500-2
	500	4		$\mathbf{D}_{\mathrm{T}}$-500-4
	750	2		$\mathbf{D}_{\mathrm{T}}$-750-2
Chemical (C)	HCl (nM) aq. sol.			
	1			$\mathbf{D}_{\mathrm{C}}$-1M
	2			$\mathbf{D}_{\mathrm{C}}$-2M
	4			$\mathbf{D}_{\mathrm{C}}$-4M
Thermo-chemical (TC)	*T* (°C)	Time (h)	HCl (2M)	
	250	2	2	$\mathbf{D}_{\mathrm{TC}}$-250-2M
	500	2	2	$\mathbf{D}_{\mathrm{TC}}$-500-2M
	750	2	2	$\mathbf{D}_{\mathrm{TC}}$-750-2M
Ultrasonic (U)	Power (W)	Time (min)		
	100	5		$\mathbf{D}_{\mathrm{U}}$-100-5
	100	10		$\mathbf{D}_{\mathrm{U}}$-100-10
	100	15		$\mathbf{D}_{\mathrm{U}}$-100-15
	100	8		$\mathbf{D}_{\mathrm{U}}$-100-8
	120	8		$\mathbf{D}_{\mathrm{U}}$-120-8
	140	8		$\mathbf{D}_{\mathrm{U}}$-140-8

In order to establish the potential reuse of the spent diatomite, three regeneration methods were considered for the raw diatomite sample, namely thermal, acid and water. In case of HCl and distilled water regeneration a solid : liquid ratio of 1:10 was used with samples under continuous stirring at 50 rpm (three-dimensional shaker) for 5 h. Three regeneration-adsorption cycles were realized in each case.

II.3.3. The results of the removal of organic dyes Toluidine Blue, Malachite Green and Congo Red from aqueous solutions using Diatomite

II.3.3.1. *Toluidine Blue*

II.3.3.1.1. The use of processed diatomite (D) for TB removing from aqueous solution

a) *Initial concentration of* **TB**

The influence of the initial concentration (C_0) of the aqueous solution of TB on the adsorption capacity of D was investigated for values within the range 10-70 mg / L. It was thus observed increase in the adsorption capacity, with the increase of the initial concentration of TB.

The maximum capacity of adsorption of D was 1.38 mg / g and removal efficinecy of TB was 99% at an initial concentration of 70 mg/L. The above data have suggested the possibility of successfully using processed diatomite (so treated) even in the case of high concentrations of dye in the effluent.

b) *Adsorbent quantity*

The influence of the adsorbent quantity, in the TB retention process, has been studied for values of 1, 2.5, 5 and 7.5 g in contact with 100 mL of TB with a concentration of 50 mg / L.

Thus, increasing the amount of D showed a decrease in the adsorption capacity due to the fact that, for the same initial concentration, has been available an increasing amount of adsorbent, and therefore a larger surface area of the solid-liquid contact. The maximum removal efficinecy was 99% in the case of using 5 g of adsorbent.

c) *Adsorbent grain size*

Study the effect of various grain sizes of the processed diatomite adsorbent (D) indicated that the retention reached a maximum efficiency, 99% to a particle size of 0.60-1.00 mm.

II.3.3.1.2. The use of treated diatomite (D) for TB removing from aqueous solution

For each considered treatment applied to the raw diatomite sample maximum removal efficiencies were considered and compared. In the case of thermal treated samples, a small increase in removal efficiency, from 71 to 77%, was observed for D-250-2 sample. This fact might be attributed to the fact that at low temperatures water is removed from the solid surface, making pores more accessible. Further increase of the temperature led to the mechanical destruction of the porous structure and therefore to a decrease of the surface available for adsorption and a removal efficiency of 58% for D-750-2 sample. When calcination time was increased from 1 to 4 hours at 500°C, the decrease in removal efficiency was constant irrespective to the calcination time (71 to 57%).

When chemical treatment was considered, a slight increase in removal efficiency was observed for D-2M sample (from 71 to 76%), while with a further increase of the HCl concentration, D-4M sample, removal efficiency dropped to 67%. This decrease might be due to the reaction occurring between the acid and the metal oxides on the adsorbent surface, reaction products blocking the pores of the diatomite, thereby reducing adsorption efficiency.

Thermo-chemical treatment of the raw diatomite did not show a positive trend on improving its adsorption capacity. The removal efficiency values decreased from 71 to 57% for D and D-750-2M, respectively.

In the case of ultrasonic treatment, increasing of power and treatment time led to the same trend in removal efficiency evolution. The best results, with a removal efficiency of 76% were obtained in case of both D-100-10 and D-120-8 samples. Further increase of time (> 10 min) and power (> 120 W) could have as a result pores destruction and therefore a decrease in removal efficiency values.

Between the considered treatments applied to the raw diatomite (Figure 10), improvements in terms of removal efficiency by comparison with D sample were obtained in case of D-250-2, D-2M, D-100-10 and D-120-8 samples, while in case of D-250-2M a decrease of removal efficiency was recorded.

II.3.3.1.3. Diatomite regeneration

The regeneration methods used on spent diatomite samples as described above, proved to have similar results when temperature and acid were used. 500°C and repeated contact with HCl led to a drastically decrease of removal efficiency (52%) after the third regeneration-adsorption cycle. Also these two methods are quite expensive and have a high environmental impact. In case of water, a slower decrease in removal efficiency was recorded, 69, 65 and 62% after the first, second and third regeneration cycle, respectively. Depending on the dye concentration present in water and taking in account that diatomite is a low cost material, usage up to 3-5 cycles with water as regeneration agent could be a promising process for colored wastewater treatment.

II.3.3.2. *Malachite Green*

a) *Initial concentration* **MG**

An increase in C_0 of MG was accompanied by a significant increase in the adsorption capacity of D, from 0.17 mg / g to 4.77 mg / g (at the ends of the range) and efficiency (91 → 99%).

b) *Adsorbent quantity*

Increasing of the amount of adsorbent showed a decrease in the adsorption capacity, due to the fact evident that, for the same initial concentration of MG was available a larger amount of adsorbent, and thus a larger contact surface. Maximum MG removal efficiency was 99%, using 1 g of adsorbent.

c) *Adsorbent grain size*

Maximum MG removal efficiency was 99%, using a grain size of d_D = 1.00-1.60 mm. Thus, changes could be correlated with the recorded due to diffusional limitations of the MG organic cation gauge, the adsorption being carried out mainly on the outer surface of the granule of diatomite.

d) *Temperature influence*

A slight increase of adsorption efficiency was observed only with the heat, from 97% (20 ° C) to 99% (40 ° C). At temperatures above 40 ° C, the yield dropped to 94% (50 ° C) as indication of the onset of the desorption process.

II.3.3.3. *Congo Red*

a) *Initial concentration* **CR**

Increasing of the initial concentration of the adsorbent was accompanied by an increase in its adsorption qe = 0.03 → 4.61 mg / g, which has increased the removal efficiency from 59% to 96% at the ends of the range of variation of C_0.

b) *Adsorbent quantity*

Increasing of the amount of adsorbent, 0.1 → 1.0 g, resulted in a decrease of its adsorption capacity, 6.31 → 0.88 mg / g. CR removal efficiency increased with increasing the amount of adsorbent D, reaching a maximum of 90% for 1 g D.

c) *Adsorbent grain size*

Thus, it was observed that the increase in grain size increased the removal efficinecy of the CR, up to a maximum of 91% for values of 1.25-1.60 mm.

d) *Temperature influence*

As can be seen, the temperature increase caused a significant decrease in removal efficiency of CR, default and the adsorption capacity of processed diatomite, this negative trend suggesting an exothermic process. The maximum values of η and qe were 87% and 1.74 mg / g, obtained at 20 ° C.

II.3.4. Adsorption isotherms of Toluidine Blue, Malachite Green and Congo Red adsorption process using Diatomite

The adsorption isotherms for the adsorption process of TB were studied by seven initial concentration therof (10, 20, 30, 40, 50, 60 and 70 mg / L), and for MG and CR whose initial seven concentrations were 10, 25, 50, 100, 150, 200 and 250 mg / L.

If the dye selected TB, the highest value of R^2 (0.9645) was obtained in the case of the Langmuir model. As this model we adopted the description, the better the retention of TB on processed Diatomite suggesting TB monolayer coverage of the surface of the adsorbent. We note similar results in literature (Alpat et al., 2008) on the case of TB dye adsorption but on zeolite.

In case of MG only one value of determination coefficient (R^2) was greater than 0.9 (0.9740), namely the Langmuir model resulting from the application. For other models studied, R^2

values were lower than 0.7. As this model we adopted the description, the better the retention of MG dye on processed Diatomite, suggesting, as for adsorption TB, MG monolayer coverage of the surface of the adsorbent. We note similar results in literature (Wang Ariyanto, 2007) on the case of MG dye adsorption but on zeolite.

For dye CR, R^2 values obtained by applying all of the models, were lower than 0.8. However, Dubinin-Radushkevich model, with an R^2 of 0.7797, we considered that describing most satisfactory the adsorption process, suggesting a Gaussian distribution of energy on adsorbent surface D. Similar results (Acemioğlu, 2004) were previously reported in cas e of CR adsorption but on rich calcium ash.

II.3.5. Thermodynamic parameters of Toluidine Blue, Malachite Green and Congo Red adsorption process using Diatomite

The adsorption process of MG and CR by processed Diatomite has been studied in the temperature range 293-323 K which allowed us to determine the Gibbs free energy (ΔG), the enthalpy (ΔH) and entropies (ΔS).

Both processes have been favored by enthalpy ($\Delta H < 0$) but less favored entropy ($\Delta S < 0$), the absolute values of both higher thermodynamic parameters for MG with a cationic dimensions smaller than the corresponding anionic CR. ΔH values more than 84 kJ / mol revealed the physical nature of the adsorption (Errais et al., 2011; Alver and Metin, 2012), more marked in the case of MG (higher exotherm, the upper single-layer structural organization, according to the isotherm Langmuir). Negative ΔG values over the range of temperatures indicated, as expected, the spontaneous nature within the meaning of adsorption processes. In accordance with those shown in Figures 40 (MG) and 44 (CR) for the unfavorable influence on the temperature increase of the efficicency of adsorption dependence of $\Delta G = f(T)$ showed a gradual displacement of all the parameter ΔG towards less negative values.

II.3.6. Kinetics of Toluidine Blue, Malachite Green and Congo Red adsorption process using Diatomite

In order to investigate the mechanisms of retention of the dyes TB, MG and CR, the testing of the experimental data and the potential rate determining step was studied the adsorption of the validity of the classical kinetic models of pseudo-I order pseudo-II order, internal and external diffusion.

The results obtained for all considered models are presented in Table 4. The pore diffusion coefficients are 7.93×10^{-8} and 2.67×10^{-8} cm^2/s for D and D-250-2, respectively, higher values than rate determining range (10^{-11} - 10^{-13} cm^2/s). Taking into consideration all the calculated values, regression coefficient (R^2) values, the fact that in case of liquid film model the intercepts have values very close to 0, Table 4, and also the shape of the time evolution curve, we have concluded that in this particular case, liquid film diffusion could be rate-determining step.

The kinetics of the adsorption process of the dyes MG and CR has been studied for the initial concentration of their aqueous solutions of 25, 100 and 200 mg / L, at a solid: solution of 0.5 g : 10 mL and a contact time of 10-360 min.

If case of MG adsorption of the four kinetic models whose validity was analyzed, only pseudo-order kinetic model II has provided satisfactory results by similarity equilibrium adsorption capacity values q_e (exp) opposite q_e (calc). Indeed, the application of pseudo-order kinetic model I, the values qe (exp) opposite the q_e (calc) were discrepant and various internal and external diffusion models gave apart of the y values of 0.

When applying kinetic models in the CR adsorption, given its diffusion coefficient, molecular size and the very small origin ordinate we could conclude that the process was controlled by diffusion (internally and externally).

II.3.7. Conclusions

A Romanian diatomite sample subjected to various treatments (thermal, chemical, thermo-chemical, and ultrasonic) was tested in the TB, MG and CR dye removal from aqueous solutions. A thorough characterization of the diatomite sample was realized. All the analyses confirmed the siliceous nature of the diatomaceous material, presence of the pennate frustules of diatoms and the small amount of impurities. Between the considered treatments applied to the raw diatomite, improvements in terms of adsorption capacity and removal efficiency were obtained in case of: D-250-s (7.97 mg/g and 77%), D-2M and D-120-8 (7.85 mg/g and 75%), and D-100-10 (7.93 mg/g and 76%) by comparison with D (7.39 mg/g and 71%).

Regeneration of the diatomite samples was realized using thermal, acid and water methods. The results showed that when the regeneration was realized with water, the smallest decrease in removal efficiency was obtained even after three regeneration-adsorption cycles (drop of 13% by comparison with thermal regeneration where a 27% drop was recorded).

Based on the adsorption results for TB, the further study for adsorption MG and CR dyes used exclusively processing Diatomite.

Process parameters influence study, the dye initial concentration, adsorbent quantity, its granulation and the temperature gave the following results:

- **TB**: T = 20 °C, C_0 = 70 mg/L, m_D = 5 g, d_D = 0.60-1.00 mm, 99% efficiency
- **MG**: T = 20 °C, C_0 = 250 mg/L, m_D = 0.5 g, d_D = 0.60-1.00 mm, 99% efficiency

- **CR**: T = 20 °C, C_0 = 250 mg/L, m_D = 0.5 g, d_D = 0.60-1.00 mm, 96% efficiency.

Our data showed that the Langmuir isotherm better described the MG and TB adsorption process. Dubinin-Radushkevich isotherm described most accurately retaining of CR.

Thermodynamic study indicated adsorption processes of MG and CR as natural, spontaneous and exothermic.

Kinetic modeling showed that pseudo-order kinetic model II was the most appropriate to describe the phenomenon in case of TB and MG. In cae of CR the process was diffusion controlled both internally and externally.

II.4. BENTONITE USED FOR ORGANIC DYES REMOVAL FROM AQUEOUS SOLUTION

II.4.1. Preparation of modified bentonite

Four bulk samples extracted from the bentonite deposits of Oraşul Nou (Satu Mare County), Petreşti (Cluj County), Valea Chioarului (Maramureş County) and Gurasada (Hunedoara County) deposits, Transylvania, Romania, were used as adsorbents for dyes removal from wastewaters. Compositional characterization of the bentonites was realized using X-ray diffraction (XRD), scanning electron microscopy - energy dispersive X-ray spectroscopy (SEM-EDS), specific surface area (SSA) using Brunauer-Emmett-Teller method (BET) and Fourier transformed infrared spectroscopy (FTIR) analysis.

In Romania, bentonitic clays occur in various places, sometimes forming ore deposits (Brana, Avramescu, and Călugăru 1986). Some of the deposits are well-known and were partially mined in the past. The bentonitic clays used, were selected for being tested due to their properties and efficiencies related to a high degree of purity (Bedelean et al. 2010).

The bentonites were used raw and after they were subjected to several treatments in dyes adsorption process from aqueous solutions. Each bentonite sample was subjected to size-fractionation, ionic exchange with tetra-n-butylammonium bromide (organoclay) and Al-pillaring. Tetra-n-butylammonium bromide, $[CH_3(CH_2)_3]_4NBr$ (98+%), was provided by Alfa Aesar, NaOH p.a. and $AlCl_3 \cdot 6\ H_2O$ p.a. used from pillaring solution were provided by Fluka and Chimopar, respectively.

All samples were first subjected to a grinding process, followed by a size separation using a 0.2 mm sieve. First treatment employed was size-fractionation. In this case < 0.2 μm fraction of the bentonitic clay was obtained. In order to obtain this fraction, a suspension (solid:liquid ratio=1:20) of clay stirred for 24 h was separated by centrifugation at 600 rpm; the obtained supernatant was centrifuged again, this time at 7000 rpm; the separated solid sample was then dried at 80°C for 24 hours (Costanzo 2001; Arroyo el al. 2005). Size-fractionated samples were obtained in this case.

In order to obtain the organoclay, raw and size-fractionated samples in suspension (solid:liquid ratio=1:100, 24 h stirring) were contacted with the organic salt under stirring for 2 h. Modified bentonite samples were prepared by adding tetra-n-butylammonium bromide to 100% cation exchange capacity of the considered clays (raw and size-fractionated). Treated clay samples were then separated by settling and washed several times until bromide-free with distilled water by centrifugation and finally dried at 60°C (24 h) (Anirudhan and Ramachandran 2006; Park, Ayoko, and Frost 2011). Organoclays on raw and size-fractionated samples were obtained.

The preparation of Al-pillared clays was carried out using dry pillaring method (clay was added as solid to the pillaring solution) (Barrault et al. 1998). In an $AlCl_3$ solution (0.2 M) kept at room temperature and stirred vigorously, NaOH solution (0.2 M) was added dropwise until the molar ratio of OH/Al = 2 was reached. The mixture, pillaring solution, was continuously stirred at room temperature for another 24 h. Size-fractionated clay sample was added into the pillaring solution mentioned above in order to obtain an Al/clay ratio of 10 mmol/g. The obtained suspension was continuously stirred for another 24 h at room temperature. The solid was recovered by centrifugation at 5000 rpm and washed until chloride-free, dried at 60°C and finally calcined at 500°C for 2 h with a heating rate of 4°C/min (Gu et al. 2011).

II.4.3. The results of the removal of organic dyes Toluidine Blue, Malachite Green and Congo Red from aqueous solutions using Bentonite

Maximum removal efficiencies and adsorption capacity values obtained during the removal of cationic and anionic dyes on the considered bentonite samples were analyzed for all samples.

In case of Oraşul Nou bentonite samples, the maximum efficiencies for all considered dyes were obtained on Oraşul Nou size-fractionated sample (Figure 10), with the highest value 92.81% in case of malachite green removal. If we compare these values for toluidine blue, malachite green and Congo red, it is easy to observe that cationic dyes are adsorbed in a higher proportion for all Oraşul Nou samples. Adsorption capacity values calculated for Oraşul Nou size-fractionated sample are 34.42, 39.12 and 12.96 mg/g for toluidine blue, malachite green and Congo red, respectively. For Valea Chioarului bentonite samples, the maximum efficiencies 99.94%, 98.92% were obtained for toluidine blue and malachite green, while in case of Congo red the best value was 16.72%. In terms of adsorption capacity, the highest calculated values were 41.03 and 41.71

mg/g, for toluidine blue and malachite green, respectively and 6.28 mg/g for Congo red. In this situation, Valea Chioarului raw and size-fractionated samples showed very similar values. Regarding Petreşti samples, the removal efficiencies for toluidine blue and malachite green adsorption had very similar values with a maximum at 99.91% and adsorption capacity at around 41.5 mg/g. Like in the previous case, the best samples in terms of cationic dyes removal proved to be Petreşti raw and size-fractionated samples at very small differences. The adsorption results in case of the last set of samples, from Gurasada, are presented in Figure 11. Gurasada size-fractionated sample proved to be the best adsorbent for all considered dyes, with removal efficiencies of 99.97, 90.81 and 59.56% in case of toluidine blue, malachite green and Congo red, respectively. Adsorption capacity values lies in 20-41 mg/g interval.

When removal efficiency for all the considered dyes on the same sample, the size-fractionated one, which proved to be better in most of the cases, Figure 12, were compared, it has been concluded that in case of cationic dyes, there are no notable differences. Between the four, Oraşul Nou size-fractionated sample showed slightly smaller values in terms of removal efficiency. By comparison in case of the anionic dye all clay samples showed removal efficiencies under 60%. This fact can be attributed to the cationic exchange capacity of the clay samples, which favors the removal of cationic dyes from aqueous solution. In case of the anionic dye, weak interactions between the electron pairs from their structure and areas with isomorphous replacements from the clay surface could be responsible for the adsorption. Also due to the fact that Congo red molecule is very big, will block pores entrance. Thus other molecules will not be able to further use the internal surface of the clay.

Evolution of the removal efficiencies and adsorption capacity values during the adsorption of cationic and anionic dyes process on bentonite samples from Oraşul Nou are next presented. Also between the considered treatments, size-fractionation proved to have as a result the best adsorbent material. Taking into consideration all the results, the following series was depicted ON-s > ON > ON-s-TBAB > ON-s-Al in terms of dye adsorbed and removal efficiency. Taking into consideration the fact that the differences in efficiency for ON-s and ON raw sample were very small (costs involved in size-separation are not justified by the increase in removal efficiency) the study was further conducted using ON sample.

The adsorption capacities and maximum removal efficiencies values obtained in case of ON sample for all considered dyes revealed that cationic dyes, TB and MG are better retained on the ON sample, 78 and 93%, and, 33 and 39 mg/g, respectively, by comparison with anionic dye CR, 25% and 9 mg/g. The negative charged sites on the bentonite surface will favor the adsorption of cationic dyes. For CR, interactions between the electron pairs from their structure and areas with isomorphous replacements from the clay surface could be responsible for the adsorption. Also CR molecule is very big, it might block pores entrance, therefore other molecules from solution will not be able to reach the internal surface.

Depending on the working conditions, deposit and the type of bentonite (Ca-, Na-, activated, organoclay), other studies report adsorption capacity values for MG ranging from 7.72 mg/g up to 176.9 mg/g, while in case of Congo red values from 7 mg/g up to 157.2 mg/g were reported. Limited studies were performed in case of TB aqueous solution – clay mineral system, one reports monolayer capacity up to 0.386 mmol/g, the other one covers the mechanism of metachromatic interaction.

Time evolution of dyes concentration during the adsorption process showed a steep decrease in concentration in the first 15 min. A decrease towards the initial concentration in 13-90% range was recorded for the concentrations in 50-200 mg/L range. The higher decrease was recorded in case of the smallest concentration. After 15 min, the concentration slowly decreases towards the equilibrium that was reached after 240 min.

In order to test the ON sample dyes removal capabilities, various concentrations in 10-250 mg/L range were also considered, using a solid : liquid ratio of 0.1:10 g/mL.

Adsorption capacity increases with concentration for all considered dyes, showing that the considered bentonite sample is able to retain high quantities of dyes and can be used when highly polluted waters should be treated with removal efficiency up to 99%.

The experiments realized using various solid : liquid ratios for TB adsorption on ON, showed that with a decrease of solid : liquid ratio, adsorption capacity increases up to a ratio of 0.025:10 g/mL, after that a slow decrease was observed.

Effect of the temperature over the adsorption process was studied in the 20-60°C interval. An increase of the adsorption capacity with temperature was recorded, for example from 33 to 40 mg/g in case of TB in the considered interval, suggesting the endothermic nature of the dye adsorption process on ON.

II.4.4. Adsorption isotherms of Congo Red adsorption process using raw Bentonite

Four adsorption isotherms, Langmuir, Freundlich, Dubinin–Radushkevich, and Temkin, were used to model the experimental data for dye adsorption on ON bentonite sample. The data collected from the experiments have been fitted to the isotherms and the calculated parameters of the adsorption isotherms obtained through linear regression for CR adsorption. According to the values of the coefficients of determination (R^2), Langmuir and Freundlich are both linear, but < 1 value of 1/n, indicated a favorable adsorption. Free energy per molecule of adsorbate values, *E*, calculated from Dubinin–Radushkevich model are in all cases smaller than 8 kJ/mol indicating a physisorption process.

II.4.*5.* Thermodynamic parameters of Toluidine Blue, Malachite Green and Congo Red adsorption process using raw Bentonite

The thermodynamic parameters reflect the feasibility and spontaneous nature of the adsorption process. Experimental results were used to calculate the thermodynamic parameters such as the Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and entropy change ($\Delta S°$) of the adsorption process of TB on ON sample. The value of $\Delta G°$ is negative and the negative value decreases with increase of temperature, suggesting that adsorption is spontaneous and is more favorable at higher temperatures. The value of enthalpy ($\Delta H°$) is positive, indicating the endothermic nature of the adsorption process.

II.4.6. Kinetics of Toluidine Blue adsorption process using raw Bentonite

Pseudo-first-order, pseudo-second-order, intra-particle, and liquid film diffusion models were used to describe the adsorption process. The kinetic parameters (q_e, k_1 and k_2) and the coefficients of determination (R^2) determined by linear regression were exemplified for TB adsorption. Taking in account the R^2 values and comparing the experimental and calculated adsorption capacity it can be concluded that pseudo-second-order kinetic model is more suitable for describing the adsorption behavior of TB onto ON. Intra-particle and liquid film diffusion models do not satisfy the zero intercept conditions therefore they not play a significant role (rate determining step) in the adsorption process. Similar results were obtained for Rhodamine B on kaolinite and montmorillonite, methylene blue and malachite green on Moroccan clay.

II.4.7. Conclusions

Four bentonite samples from Oraşul Nou, Valea Chioarului, Petreşti and Gurasada deposits (Transylvania, Romania) in various forms (raw, size-fractionated, organoclay and Al-pillared) were tested for cationic (toluidine blue, malachite green) and anionic (Congo red) dyes removal from model solutions.

Physico-chemical and mineralogical analyses of the Oraşul Nou, Valea Chioarului, Petreşti and Gurasada samples indicated that all sample rocks have montmorillonite as the main mineral constituent. XRD, SEM-EDS, BET and FTIR analyses confirmed that the treatments were applied with success.

Clay samples studied proved to be very efficient for the removal of organic dyes (toluidine blue and malachite green) from aqueous solutions, while in case of the considered anionic dye, Congo red, the results showed that adsorption on clays is not an efficient process. Also, taking into consideration all the treatments applied and the removal efficiency values obtained, the overall conclusion is that raw and size-fractionated bentonites are very good adsorbents that can be used to remove cationic dyes from aqueous solutions at concentration levels under the maximum allowable limit, therefore expensive treatments are not justified for an industrial application.

Bentonite sample from Oraşul Nou in raw and treated forms have been successfully used for cationic (TB and MG) and anionic (CR) dyes removal from aqueous solution. All investigations techniques utilized in this study lead to the same conclusion, i.e. the dyes were strongly adsorbed on the bentonite samples. Taking into consideration the adsorbed amount and removal efficiencies the following series was depicted: ON-s > ON > ON-s-TBAB > ON-s-Al.

The results included in this study show that bentonite, a low cost material, widely available in Romania, has high ability to remove especially cationic dyes from aqueous solutions and therefore is suitable for application in wastewater treatment in case of colored effluents.

II.5. CARBON XEROGEL USED FOR TOLUIDINE BLUE REMOVAL FROM AQUEOUS SOLUTION

II.5.1. Carbon Xerogel preparation

Carbon xerogel (XC) doped with K^+ cations (K-XC) was obtained by a sol-gel process (amended by Coteţ et al., 2013) as shown in Scheme 9. The process consisted of polycondensation of 2,4-dihydroxybenzoic acid (ADHB) partly neutralized as salt and potassium, with formaldehyde in the presence of K_2CO_3.

K-XC was then subjected to a grinding process followed by separation to obtain the size fraction with grain size <0.25 mm.

II.5.3. The results of the removal of Toluidine Blue from aqueous solutions using Carbon Xerogel

a) *Initial concentration* **TB**

Thus, in Figure 67 is shown the evolution of the TB concentration decreasing in time, Adsorption-desorption thermodynamic equilibrium is established after about 360 min, regardless of the initial value 10, 25 or 50 mg / L.

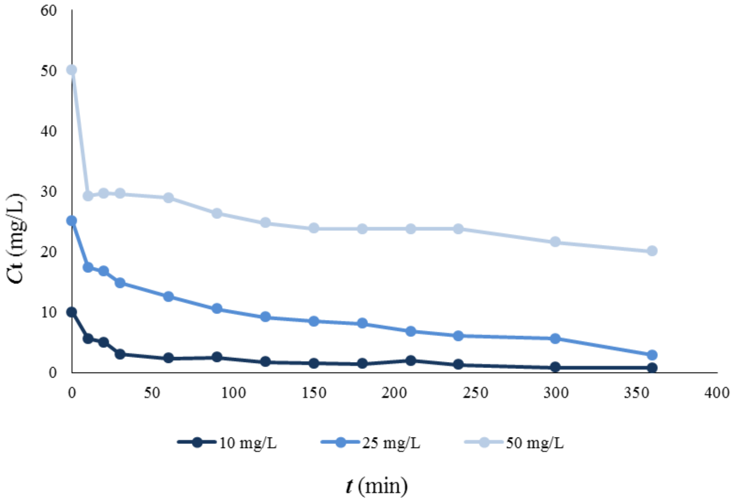


Figure 67. Concentration evolution in time
(*conditions*: T = 20 °C; $m_{K\text{-}XC}$ = 0.05 g; V = 10 mL **TB**; $d_{K\text{-}XC}$ < 0.25 mm; t = 360 min)

After a efficiency increase (75 → 79%), the range of concentrations 10-25 mg / L TB, there was a sharp decrease (38%, C0 = 50 mg / L), which was subsequently continued (38 → 10%) with increasing concentration (50 → 250 mg / L TB).

b) *Adsorbent quantity*

η values increased continuously relative to K-XC quantity seen in the two sharp positive developments (23 → 45% for 0.02 and 0.03 g and 45 →75% for 0.03 → 0.04 g K-XC). TB maximum removal efficiency (79%) was achieved using 0.05 g K-XC after that, even at its doubling, on η changes were not significant. The adsorption capacity values of the K-XC were 5.55 mg / g (0.01 g) and 2.01 mg / g (0.1 g), observing their decrease with increasing amounts of adsorbent.

c) *Temperature influence*

A significant increase in efficiency due to heating, from 79% (20 ° C) to 97% (50 ° C), endothermic nature of the adsorption process is thus deduced default. The adsorption capacity values of the K-XC were 3.94 mg / g (20 ° C) and 4.65 mg / g (50 ° C). When temperature exceeding 50 ° C, there was a noticeable decrease in the efficiency, therefore, most likely less pronounced movement in the direction of adsorption equilibrium.

II.5.4. Adsorption isotherms of Toluidine Blue adsorption process using Carbon Xerogel

Equilibrium modeling was performed for TB initial concentrations in the range of 10-250 mg / L at a temperature of 20 ° C for 360 min.

A value of determination coefficient (R^2) of more than 0.9000 was obtained only in the case of Dubinin-Radushkevich model (0.9417), it is therefore considered as a best describing the process under consideration suggesing a Gaussian distribution of energy on adsorbent surface. We note, similar results reported for Direct Red 224 dye adsorption on carbon nanotubes (Kuo et al., 2008).

II.5.5. Thermodynamic parameters of Toluidine Blue adsorption process using Carbon Xerogel

According to the Figure 70, the TB adsorption on the K-XC has been studied in the temperature range 293-333 K which allowed us to determine the Gibbs free energy (ΔG), enthalpy (ΔH) and entropy (ΔS).

The positive value of the enthalpy ($\Delta H = +20.52$ kJ / mol) was confirmed as one endothermic process of physical, $\Delta H < 84$ kJ / mol (Alver and Metin, 2012). The positive change in entropy, ΔS, showed an increase in disorder at the solid-liquid interface during the adsorption process, the degree of freedom of the adsorbed species (Alver and Metin, 2012). Finally, ΔG related data revealed a spontaneous restraint process in the sense adsorption equilibrium favored entropic.

II.5.6. Kinetics of Toluidine Blue adsorption process using Carbon Xerogel

In the case of applying pseudo-order kinetic model I, the adsorption capacity calculated values q_e (calc.), (0.88-2.14 mg / g) were clearly different from the experimental q_e (exp.) (1.54-5.24 mg / g).

Instead, order kinetic model pseudo-II has provided us with results. Thus, in this case, the values q_e (calc.) (1.59, 4.38 and 5.22 mg / g) was very close to the experimental q_e (exp.) (1.54, 4.24 and 5.24). Then, the values of R^2 within the range 0.9799-0.9933 were the closest one of all the models studied. In conclusion, the pseudo-order kinetic model II was the one that most closely described the TB adsorption phenomenon on K-XC, suggesting that the rate determining step was adsorption.

II.5.7. Conclusions

Carbon xerogel doped with K^+ cations, obtained by a sol-gel process was tested as adsorbent in adsorption process of TB from aqueous solution.

The study of the influence of various adsorption process parameters (initial concentration, adsorbent quantity and temperature) led us to obtain a maximum removal efficiency of 97%, under the conditions 50 ° C, 25 mg / L, 0.50 g, 10 ml of TB, 360 min.

In the case of thermodynamic equilibrium modeling Dubinin-Radushkevich isotherm showed that best describe the studied phenomenon, by means of a Gaussian power distribution of TB on the surface of the adsorbent.

Thermodynamic study of the retention of the TB dye on the K-XC set as one spontaneously in the sense of the adsorption, endothermic and entropic controlled.

Kinetic modeling of the process validated in its entirety, the pattern of the pseudo-second order.

CHAPTER III. ORIGINAL CONTRIBUTIONS.

ORIGINAL CONTRIBUTIONS. STUDIES ON PHENOL REMOVAL, FROM AQUEOUS SOLUTION, FROM DESTRUCTIVE METHODS: CATALYTIC WET AIR OXIDATION

1. "*Novel metal modified diatomite, zeolite and carbon xerogel catalysts for mild conditions wet air oxidation of phenol: Characterization, efficiency and reaction pathway*"
Raluca Pleşa Chicinaş, Emese Gál, Horea Bedelean, Mircea Darabantu, Andrada Măicăneanu
Separation and Purification Technology, **2018**; 197: 36–46.

2. "*Preparation, characterization, and testing of metal-doped carbon xerogels as catalysts for phenol CWAO*"
Raluca Pleşa Chicinaş, L. Cosmin Cotet, Andrada Măicăneanu, Mihai Vasilescu, Adriana Vulpoi *Environmental Science and Pollution Research*, **2017**; 24: 2980–2986.

3. "*Catalytic wet air oxidation of phenol using metal modified zeolitic volcanic tuffs*"
Raluca Pleşa Chicinaş, Zoltán Zsebe, Horea Bedelean, Mircea Darabantu, Andrada Măicăneanu
Studia UBB Chemia, LX, **2015**; 3: 237-246.

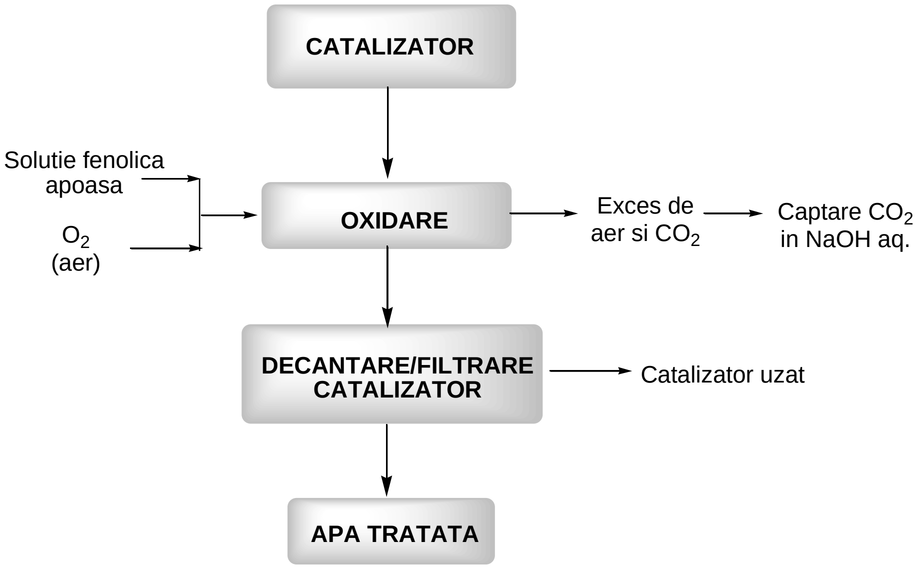
ABSTRACT

Chapter III presents structural characterisation methods (determined by techniques SEM-EDX, TEM, XRD, FTIR, and adsorption-desorption of N_2) of the zeolitic volcanic tuff and diatomite, both modified with metals and those of the carbon xerogel doped with metals, for use as catalysts in the catalytic wet air oxidation (CWAO) of phenol from aqueous solution. CWAO process efficiencies are discussed as a result of the influence of various factors: the nature of the metal, the process, initial phenol concentration, air flow rate, the amount of catalyst, temperature and grain size of the catalyst. After establishing the optimal conditions we try to identify reaction possible ways for each group of catalysts separately.

Keywords: CWAO, phenol, diatomite, zeolitic volcanic tuff, carbon xerogel

III.1. INTRODUCTION

As indicated in Section I (I.3), the overall sequence of operations in the catalytic wet air oxidation (CWAO) of phenol is shown in Scheme 1.



Scheme 1. Catalytic wet air oxidation of phenol process

Depending on the particle size of the catalyst, the catalytic wet air oxidation of phenol was carried out in two reactors, each thermostated, in a semi-continuous process: in a reactor provided with stirring (d < 0.2 mm) and in a fixed bed reactor (d = 0.2-0.8 mm). Semi-continuous regime is in case were the reactor was continuously fed to the air, which has a constant input flow, a priori set, and the aqueous phenol solution was added to the reactor until the beginning of the experiment, thus discontinuously.

III.2. MATERIALS AND METHODS

III.2.1. Materials

Zeolitic Volcanic Tuff (**TVZ**) and Diatomite (**D**) has the same origins like those from Chapter II (Sections II.1.1.1 şi II.1.1.2.).

III.2.2. Analytical methods

Zeolitic volcanic tuff modified with metals (Me-TVZ), diatomite modified with metals (Me-D) and carbon xerogels doped with metals (Me-XC) were investigated by techniques TEM, SEM-EDX, XRD, FTIR and S_{BET}.

III.3. METALS MODIFIED ZEOLITIC VOLCANIC TUFF USED AS CATALYSTS FOR PHENOL REMOVAL FROM AQUEOUS SOLUTION BY CATALYTIC WET AIR OXIDATION

III.3.1. Metals modified zeolitic volcanic tuff preparation

The raw Zeolite sample was crushed, grounded and passed through mesh sieves (0.4-0.6 mm fraction was collected, selected based on preliminary tests using a series of grain sizes). Then, the Zeolite sample was washed with distilled water, dried at 105°C for 24 h. Dried sample was then treated, at pH = 10 (NaOH), with a 1 M NaCl aqueous solution under stirring (330 rpm) for 2 h with a solid : solution mass ratio of 1:10. Finally, the resulted sample was washed with distilled water (until chlorine anions were no longer detected with $AgNO_3$) and dried at 105°C for 24 h (modified after Mondale et al. 1995 and Panayotova et al. 2003). The resulted Na-TVZ form of the Zeolite was thus obtained and further used. This preliminary cationic exchange was included in the catalyst preparation process based on previously reported data that demonstrate the higher efficiency of the Na modified Zeolite (Na-TVZ) form with respect to the raw Zeolite sample.

Next, Na-TVZ sample was subjected to a cation exchange process, as described in our previous work, upon treatment with a 0.5 N aqueous solution containing the same selected metal cations and solid : solution mass ratio as in the case of Diatomite. The cationic exchange procedure was conducted using a 3D shaker (50 rpm) for 24 h. After that, samples were separated from the precursor solution by settling, washed several times with distilled water, dried at 105°C (24 h) and calcined 250°C (4 h, with a heating rate of 4°C/min). The Me-TVZ catalysts thus obtained are listed in Table 1.

Tabelul 1. Me-TVZ catalysts

Me(a-d)-TVZ	Precursors	$d_{a\text{-}d}$ (mm)
Cu(a1)-TVZ	$CuSO_4 \cdot 5H_2O$	$d_a < 0.2$ (**a**)
Cu(a2)-TVZ	$Cu(NO_3)_2 \cdot 3H_2O$	
Ni(a)-TVZ	$Ni(NO_3)_2 \cdot 6H_2O$	
Zn(a)-TVZ	$Zn(NO_3)_2 \cdot 6H_2O$	
Co(a)-TVZ	$Co(NO_3)_2 \cdot 6H_2O$	
Mn(a)-TVZ	$Mn(NO_3)_2 \cdot 4H_2O$	
Ce(a)-TVZ	$Ce(NO_3)_3 \cdot 6H_2O$	
Fe(a)-TVZ	$Fe(NO_3)_3 \cdot 9H_2O$	
Cu(b)-TVZ	$CuSO_4 \cdot 5H_2O$	$d_b = 0.2\text{-}0.4$ (**b**)
Cu(c1)-TVZ	$CuSO_4 \cdot 5H_2O$	$d_c = 0.4\text{-}0.6$ (**c**)
Cu(c2)-TVZ	$Cu(NO_3)_2 \cdot 3H_2O$	
Ni(c)-TVZ	$Ni(NO_3)_2 \cdot 6H_2O$	
Zn(c)-TVZ	$Zn(NO_3)_2 \cdot 6H_2O$	
Co(c)-TVZ	$Co(NO_3)_2 \cdot 6H_2O$	
Mn(c)-TVZ	$Mn(NO_3)_2 \cdot 4H_2O$	
Ce(c)-TVZ	$Ce(NO_3)_3 \cdot 6H_2O$	
Fe(c)-TVZ	$Fe(NO_3)_3 \cdot 9H_2O$	
Cu(d)-TVZ	$CuSO_4 \cdot 5H_2O$	$d_d = 0.6\text{-}0.8$ (**d**)

III.3.3. The phenol removal results from aqueous solutions by Catalytic Wet Air Oxidation using metals modified zeolitic volcanic tuff as catalyst

III.3.3.1. *General conditions*

In case of thermostated stirring reactor the typical experiment was conducted under the following conditions: 100 ml aqueous phenol concentration of 1000 mg / L and 4 g of catalyst were introduced into the reactor and the stirring was kept at 500 rot / min. The reaction temperature was 60 ° C at an air flow rate of 60 L / h for 360 min. The analogous experiment without catalyst (WAO - Wet Air Oxidation) as in the presence of Na- TVZ, were carried out under the same reaction conditions. All the experiments were performed in triplicate (±2% reproducibility), the hereafter discussed data being averaged values.

In order to establish the optimal conditions for the oxidation process of phenol in the thermostated reactor, with stirring, studied the influence of the following factors: the nature of metal, time (t, 180-360 min), initial phenol concentration (250-1250 mg / L), the air flow (20-70 L / h), the amount of catalyst (1-2.5 g) and the temperature (40-60 ° C).

CWAOs of phenol carried out in a thermostated fixed bed reactor (air flows continuously through the tube that contains the fixed bed of catalyst, which is immersed in the phenol aqueous solution), placed on a 3D shaker (50 rpm), at atmospheric pressure by using throughout 25 mL phenol solution, 1 g catalyst and 360 min reaction time. Various reaction conditions were used: temperature (50-70°C), phenol initial concentration (750-1250 mg/L) and 20-40 L/h air flow (space time 0.074-0.15 sec). Typical conditions were: 60°C, 1000 mg phenol/L and 20 L/h air flow. A blank sample, **Na-TVZ**, was also tested in the same conditions. All the experiments were performed in triplicate (±2% reproducibility), the hereafter discussed data being averaged values.

The evolution of phenol oxidation process was evaluated by means of efficiency, calculated using $KMnO_4$ Chemical Oxygen Demand (COD, mg $KMnO_4$/L) values. They were obtained for the initial solution (COD_i) and at the end of CWAO reaction (COD_f), using eq. (1).

$$E_{COD}\,(\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \qquad \text{(Eq. 1)}$$

III.3.3.2. *Phenol CWAO results using thermostated batch reator*

a) *Metal influence*

Experimental data allowed us to establish the following hierarchy of decreasing efficiency type samples: **Me(a)-TVZ**: **Cu(a1)-TVZ** > **Fe(a)-TVZ** > **Zn(a)-TVZ** > **Mn(a)-TVZ** > **Ce(a)-TVZ** ≈ **Co(a)-TVZ** > **Cu(a2)-TVZ** > **Ni(a)-TVZ** > **Na(a)-TVZ**.

Maximum efficiency, 33.7%, with corresponding to **Cu**(**a1**)**-TVZ** sample, decided to select it for investigate its catalytic abilities, further, in accordance with influencing factors mentioned above (Section III.3.3.1).

b) *Time influence*

The influence of this factor on the CWAO of phenol has been studied for the durations of 180, 240, 300 and 360 minutes. It has been observed an increase of the oxidation process efficiency (which reached a maximum of 33.7% at 6 hours) with increasing of reaction time.

c) *Phenol initial concentration influence*

Initial concentrations of the phenol solution were 250, 500, 750, 1000, and 1250 mg / L. With the increase of the initial concentration of phenol to 1000 mg / L, growth took place, in parallel, the COD values. To overcome this limitation of the initial concentration, we observe a decrease in the efficiency of diffusional limitations due to the possible oxidation-induced increase in the number of molecules of phenol relative to the available surface area of the catalyst.

d) *Air flow influence*

The influence of this parameter was examined for the values of 20, 30, 40, 50 and 60 L / h, the other conditions being identical to the previous conditions. The maximum efficiency of the process, 33.7%, was achieved at an air flow rate of 60 L / h. Increase air flow over this value resulted in a decrease of the COD, which might limit the diffusion of oxygen to the catalyst surface and thus its adsorption.

e) *Catalyst quantity influence*

Increasing the amount of catalyst, up to 4 g, COD values was reflected in the increase, due to increasing the number of active centers on its surface. To further increase the amount of catalyst (5 g) was observed decrease in the COD value (default efficiency) of the oxidation process, most likely due to agglomeration of the catalyst particles, with the result that there is a limitation reactants access to the active centers.

f) *Temperature influence*

It can be seen that the COD values increased with increasing of reaction temperature. The process of any exothermicity of the oxidation conditions, the positive influence on the efficiency of the temperature increase was due obviously to the kinetic factors consisting of accelerating the chemical activation process at the same time.

III.3.3.3. *Phenol CWAO results using thermostated fixed bed reactor*

COD efficiencies of the phenol CWAO process, carried out in the presence of **Me-TVZ** catalysts in fixed bed reactor. COD values ranged between 22-54%, with a maximum in the case of **Cu**(**b**)**-TVZ**, 54%. The following series in decreasing order of the COD efficiencies was established: **Cu**(**b**)**-TVZ** > **Ce-TVZ** > **Zn-TVZ** > **Ni-TVZ** ≈ **Cu**(**a**)**-TVZ** > **Co-TVZ** > **Fe-TVZ** ≈ **Mn-TVZ** > **Na-TVZ**. Therefore, in order to study the influence of the reaction parameters over the CWAO reaction, Copper modified Zeolite, **Cu**(**b**)**-TVZ**, was the catalyst of choice.

Main observations are resumed below:

(i) The maximum COD efficiency obtained at 60°C was 54% (Figure 8). By increasing the temperature at 70°C, COD efficiency value decreased.

(ii) If the air flow was increased over 30 L/h, the COD efficiency decreased.

(iii) Starting from 750 mg/L, an increase of phenol initial concentration led to an increase of the COD efficiency up to 1000 mg/L, 62%. If the phenol initial concentration was further increased, i.e. at 1250 mg/L, a decrease of COD efficiency was noticed.

To conclude, the highest COD efficiency obtained for phenol CWAO using **Cu**(**b**)**-TVZ** as catalyst, was 62%, achieved under the following reaction conditions: temperature (60°C), phenol initial concentration (1000 mg/L), air flow (30 L/h), **Cu**(**b**)**-TVZ** amount (1 g), and reaction time (360 min).

III.3.4. Conclusions

Zeolitic volcanic tuff (TVZ) collected from the deposit Măcicaş (County. Cluj), was modified by means of an overall process of cation exchange form TVZ → Na-TVZ → Me-TVZ, metal (**Me^{n+}**: Na^+, Cu^{2+}, Co^{2+}, Ce^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+} şi Zn^{2+}) by using different grain size (d) of the TVZ (d <0.2, 0.2-0.4, 0.4-0.6 and 0.6-0.8 mm). TVZ modified metal samples were characterized by SEM-EDX, TEM, XRD, FTIR and S_{BET} techniques. Major structural aspects observed consisted of (i) the identification of each sample analyzed Me-TVZ, the presence of metal (Me^{n+}) modifier, and (ii) maintain the integrity of their porosity TVZ, calcination.

Me-TVZ samples were tested as catalysts in the catalytic wet air oxidation (CWAO) of phenol from aqueous solution.

Depending on the particle size of the catalyst, the reaction was carried out in two reactors, namely the semi-continuous thermostated reactor with stirring and semi-continuous thermostated reactor with fixed bed.

As a result of a preliminary selection of Me-TVZ study of the influence of specific parameters of the process CWAO, the reaction time (t), the initial concentration of the aqueous solution of phenol, the air flow, the amount of catalyst and temperature was focus on the sample **Cu**(**a1**)-**TVZ** ($d_{a1} < 0.2$ mm) in the case of thermostated reactor, with stirring and on the sample **Cu**(**c1**)-**TVZ** ($d_{c1} = 0.4\text{-}0.6$ mm) in the case of thermostated reactor, with fixed bed.

In the case of thermostated reactor with stirring, the maximum efficiency of CWAO process of phenol, 33.7% (units COD) has been reached under the conditions: T = 60 ° C, C_0 = 1000 mg phenol / L, Q = 60 L / h, *m*[**Cu**(**a1**)-**TVZ**] = 4 g, t = 360 min.

In the case of thermostated reactor with stirring, the maximum efficiency of CWAO process of phenol, 53.9% (units COD) has been reached under the conditions: T = 60 °C, C_0 = 1000 mg fenol/L, Q = 20 L/h, *m*[**Cu**(**c1**)-**TVZ**] = 1 g, t = 360 min.

In conclusion, the operation in a semi-continuous thermostated reactor, with fixed bed appears more advantageous with respect to the semi-continuous version, with stirring.

III.4. METALS MODIFIED DIATOMITE USED AS CATALYSTS FOR PHENOL REMOVAL FROM AQUEOUS SOLUTION BY CATALYTIC WET AIR OXIDATION

III.4.1. Metals modified diatomite preparation

The raw Diatomite sample was crushed, grounded and passed through mesh sieves ((**a**-**c**) with d_a (mm) < 0.2 (simbol **a**), d_b = 0.2-0.4 (simbol **b**) şi d_c = 0.4-0.6 (simbol **c**) mm). Next, in order to obtain the chosen catalysts, Diatomite sample was subjected to an adsorption process, upon treatment with a 0.5 N aqueous solution containing a selected metal cation (Co^{2+}, Ce^{3+}, Ni^{2+}, Fe^{3+}, Zn^{2+}, Mn^{2+} and Cu^{2+} respectively) using a solid : solution mass ratio of 1:10. The adsorption procedure was conducted in an ultrasonic bath at room temperature at 100 W power for 10 min. After the ultrasonic treatment, samples were separated from the precursor solution by settling, washed several times with distilled water, dried at 105°C (24 h) and calcined at 250°C (4 h, with a heating rate of 4°C/min).

Table 5. Metals modified Diatomite sample

Notation	Precursors	$d_{a\text{-}c}$ (mm)
(**a**)-**D**	-	$d_a < 0.2$ (**a**)
Cu(**a**)-**D**	$Cu(NO_3)_2 \cdot 3H_2O$	
Ce(**a**)-**D**	$Ce(NO_3)_3 \cdot 6H_2O$	
Fe(**a**)-**D**	$Fe(NO_3)_3 \cdot 9H_2O$	
Ni(**a**)-**D**	$Ni(NO_3)_2 \cdot 6H_2O$	
Mn(**a**)-**D**	$Mn(NO_3)_2 \cdot 6H_2O$	
Co(**a**)-**D**	$Co(NO_3)_2 \cdot 6H_2O$	
Zn(**a**)-**D**	$Zn(NO_3)_2 \cdot 4H_2O$	
(**b**)-**D**	-	$d_b = 0.2\text{-}0.4$ (**b**)
Cu(**b**)-**D**	$Cu(NO_3)_2 \cdot 3H_2O$	
(**c**)-**D**		$d_c = 0.4\text{-}0.6$ (**c**)
Cu(**c**)-**D**	$Cu(NO_3)_2 \cdot 3H_2O$	
Ce(**c**)-**D**	$Ce(NO_3)_3 \cdot 6H_2O$	
Fe(**c**)-**D**	$Fe(NO_3)_3 \cdot 9H_2O$	
Ni(**c**)-**D**	$Ni(NO_3)_2 \cdot 6H_2O$	
Mn(**c**)-**D**	$Mn(NO_3)_2 \cdot 6H_2O$	

Co(c)-D	$Co(NO_3)_2 \cdot 6H_2O$
Zn(c)-D	$Zn(NO_3)_2 \cdot 4H_2O$

III.4.3. The phenol removal results from aqueous solutions by Catalytic Wet Air Oxidation using metals modified diatomite as catalyst

III.4.3.1. *General conditions*

In case of thermostated stirring reactor the typical experiment was conducted under the following conditions: 100 ml aqueous phenol concentration of 1000 mg / L and 4 g of catalyst were introduced into the reactor and the stirring was kept at 500 rot / min. The reaction temperature was 60 ° C at an air flow rate of 60 L / h for 360 min. The analogous experiment without catalyst (WAO - Wet Air Oxidation) as in the presence of D sample, were carried out under the same reaction conditions. All the experiments were performed in triplicate (±2% reproducibility), the hereafter discussed data being averaged values.

In order to establish the optimal conditions for the oxidation process of phenol in the thermostated reactor, with stirring, studied the influence of the following factors: the nature of metal, time (t, 180-360 min), initial phenol concentration (250-1250 mg / L), the air flow (20-70 L / h), the amount of catalyst (1-2.5 g) and the temperature (40-60 ° C).

CWAOs of phenol were carried out in a thermostated fixed bed reactor (air flows continuously through the tube that contains the fixed bed of catalyst, which is immersed in the phenol aqueous solution), placed on a 3D shaker (50 rpm), at atmospheric pressure by using throughout 25 mL phenol solution, 1 g catalyst and 360 min reaction time. Various reaction conditions were used: temperature (50-70°C), phenol initial concentration (750-1250 mg/L) and 20-40 L/h air flow (space time 0.074-0.15 sec). Typical conditions were: 60°C, 1000 mg phenol/L and 20 L/h air flow. A blank sample, **D**, was also tested in the same conditions. All the experiments were performed in triplicate (±2% reproducibility), the hereafter discussed data being averaged values (Sections 3.2.1. and 3.2.2.).

The evolution of phenol oxidation process was evaluated by means of efficiency, calculated using $KMnO_4$ Chemical Oxygen Demand (COD, mg $KMnO_4$/L) values. They were obtained for the initial solution (COD_i) and at the end of CWAO reaction (COD_f), using eq. (1).

$$E_{COD}\,(\%) = \frac{COD_i - COD_f}{COD_i} \times 100 \qquad \text{(Eq. 1)}$$

III.4.3.2. *Phenol CWAO results using thermostated batch reactor*

Information, as compared to efficiencies were determined CWAO (% COD), obtained for the catalysts Cu-D (prepared by impregnating only magnetic stirring) and Cu(a)-D (prepared by impregnation under sonication), under the same reaction conditions (60 C, 60 L / h, 1000 mg / L, 100 mL, 4 g, 360 min). They were 13.4% (Cu-D) and 42.7% (Cu(a)-D), which justified the application of the impregnation process for the preparation by adsorption under ultrasonification.

a) *Metal influence*

Ctalysts could thus rank in low efficiency purposes, as follows: **Cu(a)-D** > **Ni(a)-D** > **Ce(a)-D** ≈ **Co(a)-D** > **Zn(a)-D** > **Mn(a)-D** > **Fe(a)-D** > **(a)-D**.

Efficiency values were in the range of 9.2-42.7%, the maximum corresponding to the catalyst Cu(a)-D. As it was decided further use Cu(a)-D to study the factors of influence.

b) *Initial phenol concentration influence*

The study was performed for initial concentration of phenol in the range of 750-1250 mg / L. The maximum COD value, 42.7%, was obtained for the initial concentration of 1000 mg / L.

c) *Air flow influence*

The maximum COD, 42.7% was achieved at an air flow rate of 60 L / h. In fact, with the increase in air flow, an increase of COD was observed which suggested that the diffusion of oxygen could be a rate-limiting step in the catalytic oxidation. However, a higher air flow rate of 60 L / h, 70 L / h, the COD dropped by approx. 10% of the previous maximum.

d) *Catalyst quantity influence*

Thus, increasing the amount of catalyst, up to 4 g, increased the COD values, due to increasing the number of active centers on the surface of the catalyst. However, if we increase further, the amount of catalyst (5 g), there were decreases in COD approx. 10% (and thus the oxidation process efficiency) due to the fact, most likely agglomeration of catalyst particles, the immediate consequence of limiting the diffusion of oxygen.

e) *Temperature influence*

The positive influence of temperature increase was observed until the 60 ° C (42.7% COD), with minor fluctuations of the COD (±2%) corresponding to changes in the ±10 ° C.

We note the fact that all the samples of metals modified diatomite Me-D have not been performed in order to determine optimal reaction conditions, in the thermostated reactor with fixed bed, because Diatomite (D) is a material very similar to natural zeolitic volcanic tuff (TVZ discussed in section III.3). Indeed, both are mesoporous materials having values of specific surface area and pore volume are very close and similar structural properties.

III.4.3.3. *Phenol CWAO results using thermostated fixed bed reactor*

COD efficiencies of the phenol CWAO process, carried out in the presence of **Me-D** catalysts in fixed bed reactor, were investigated. The obtained values ranged between 41-66%, with a maximum in the case of **Fe-D**. The following series in decreasing order of the COD efficiency values was determined: **Fe-D** > **Zn-D** > **Cu**(**a**)-**D** ≈ **Ni-D** > **D** > **Mn-D** > **Ce-D** > **Cu**(**b**)-**D** > **Co-D**.

III.4.4. Conclusions

Diatomite collected from Minis deposit (Arad), processed and separated into fractions of different grain size (d <0.2, 0.2-0.4, 0.4-0.6 and 0.6-0.8 mm) was modified by impregnation with metal transition (Cu^{2+}, Co^{2+}, Ce^{3+}, Fe^{3+}, Mn^{2+}, Ni^{2+} and Zn^{2+}), followed by calcination.

Metals modified Diatomite samples were initially characterized by SEM-EDX, XRD, FTIR and S_{BET}. The porous structure of diatomite was not destroyed by calcination.

The samples thus obtained were tested and characterized as catalysts in the catalytic wet air oxidation (CWAO) of phenol in aqueous solution.

For this purpose we used two types of reactors, thermostated reactor with stirring and thermostated reactor with fixed bed. The choice of a particular type of reactor has been subject to a particle size (d) diatomaceous catalyst.

In thermostated reactor, with stirring (d <0.2 mm), the study of the influence parameters (the initial phenol concentration, air flow rate, amount of catalyst and temperature) showed the sample Cu(a)-D as the most efficient (COD value of 42.7%) under the conditions: C_0 (1000 mg / L), Q (60 L / h), m (4 g catalyst) and T (60 ° C).

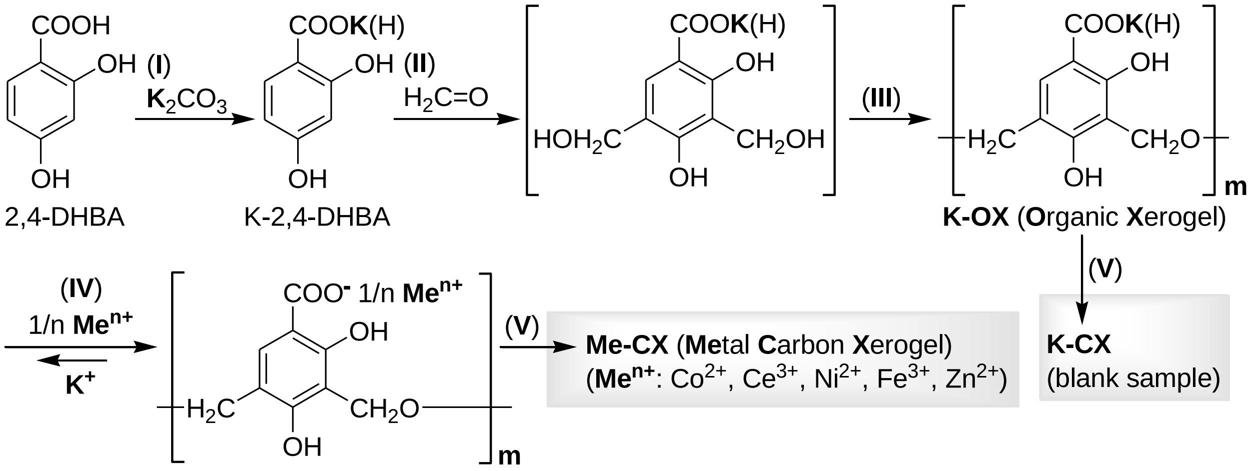
In thermostated reactor, with fixed bed (d = 0.4-0.6 mm) the best results were observed for the Fe(c)-D sample (COD 66.0%). In this case, the influence of parameters (see above) on CWAO phenol was not studied because structural characteristics between the two natural materials zeolitic volcanic tuff (TVZ) and diatomite (D) is expected a similar amount in their modified forms of the metal, Me(a-d)-TVZ vs. Me(a-c)-D.

Finally, identical to the situation encountered in the case of catalysts based on metal modified zeolitic volcanic tuff (Section III.3.4.), in the case of metals modified diatomite operation in thermostated reactor with fixed bed was recovered as the most effective.

III.5. METALS DOPED CARBON XEROGEL USED AS CATALYSTS FOR PHENOL REMOVAL FROM AQUEOUS SOLUTION BY CATALYTIC WET AIR OXIDATION

III.5.1. Metals doped carbon xerogel preparation

The chemistry followed in this study, sol-gel protocol, is resumed in Scheme 1.



Scheme 1. Preparation of Metals-doped Carbon Xerogels (**Me-CX**). *Reagents and conditions*: (**I**) aq. K_2CO_3 (0.5 equiv.), r.t.; (**II**) $H_2C=O$ (2.0 equiv.) as 37% aq. soln., K_2CO_3 (1% mol); (**III**) 70 ^oC, 72 h; (**IV**) 0.1 M aq. Me^{n+}, r.t., 3×24 h; (**V**) pyrolysis, 750 ^oC, 2 h / Ar.

First, Potassium-doped Organic Xerogel (**K-OX**) was obtained by applying the sol-gel method (**I-III**). Thus, potassium-2,4-dihydroxybenzoate (K-2,4-DHBA), obtained from the partial neutralization of 2,4-dihydroxybenzoic acid (2,4-DHBA) upon treatment with an aqueous K_2CO_3 solution (**I**) and formaldehyde were used as starting materials for the polycondensation reaction in the presence of K_2CO_3 as catalyst (**III**). The sol-gel process (**III**) took place in sealed glass bottle. The resulted wet **K-OX** doped gel was then immersed in a 0.1 M doping metal salt aqueous solution (**IV**). The immersion process was repeated 3 times at 24 hours intervals, with fresh metal salt solution. Thus, potassium cations from the wet gel were replaced by the corresponding metal through cation exchange process and the metal doped gel was obtained. This material was dried under ambient conditions (20±2°C) and then pyrolyzed (**V**) at 750°C in argon atmosphere for 2 h. The resulted Metal-doped Carbon Xerogels, **Me-CX** (**Me^{n+}**: Co^{2+}, Ce^{3+}, Ni^{2+}, Fe^{3+} and Zn^{2+}), are listed in Table SM-3. A blank **K-CX** sample was also prepared from **K-OX** using the same stages (**I-III**, **V**) described above, without the 1/n **Me^{n+} ⇆ K^+** cationic exchange step (**IV**).

Table 8. Metals doped Carbon Xerogel

Sample	Metal cation	Precursors	Solvent	No. changes / solution, mL*
K-XC	K^+	K_2CO_3	**-**	**-**
Ce(E2)-XC	Ce^{3+}	$Ce(NO_3)_3\cdot 6H_2O$	**E**tanol (**E**)	**2**/150
Co(1E2)-XC	Co^{2+}	$Co(NO_3)_2\cdot 4H_2O$		
Co(2E2)-XC	Co^{2+}	$Co(CH_3COO)_2\cdot 6H_2O$		
Ni(E2)-XC	Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$		
Co(E3)-XC	Co^{2+}	$Co(NO_3)_2\cdot 6H_2O$	**E**tanol (**E**)	**3**/150
Ni(E3)-XC	Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$		
Co(A2)-XC	Co^{2+}	$Co(NO_3)_2\cdot 6H_2O$	**A**pă bidistilată (**A**)	**2**/150
Ni(A2)-XC	Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$		
Ce(A3)-XC	Ce^{3+}	$Ce(NO_3)_3\cdot 6H_2O$	**A**pă bidistilată (**A**)	**3**/150
Fe(A3)-XC	Fe^{3+}	$Fe(NO_3)_3\cdot 9H_2O$		
Zn(A3)-XC	Zn^{2+}	$Zn(NO_3)_2\cdot 6H_2O$		
Co(A3)-XC	Co^{2+}	$Co(NO_3)_2\cdot 6H_2O$		
Ni(A3)-XC	Ni^{2+}	$Ni(NO_3)_2\cdot 6H_2O$		
Co(A3)-AC	Co^{2+}	$Co(NO_3)_2\cdot 6H_2O$		

III.5.3. The phenol removal results from aqueous solutions by Catalytic Wet Air Oxidation using metals doped carbon xerogel as catalyst

III.5.3.1. *Reaction conditions influence over phenol CWAO results*

CWAO phenol experiments were conducted in a thermostated reactor, a semi-continuous magnetic stirring, operating at atmospheric pressure. For phenol CWAO efficiency using Me-XC catalysts was used the method of total organic carbon (TOC).

Study was realised using **Co(2E2)-XC** catalyst.

a) *Phenol initial concentration influence*

Increasing the value of TOC was observed up to 40.4%, while increasing the initial phenol concentration up to 150 mg / L, followed by a significant reduction (30.3%) to a C_0 value of 175 mg / L. That could be due to diffusional limitation, caused by agglomeration of the catalytic surface phenol molecules with the increase in the initial concentration while maintaining a constant amount of catalyst.

b) *Air flow influence*

The maximum value of efficnecy (TOC 36.3%) was a consequence of the increased air flow to 40 L / h. To further increase the air flow 60 L / h, the TOC fell to 21.1%, most probably due to the diffusion of oxygen to the surface of the catalyst and adsorption in the larger air flow has been limited.

c) *Catalyst quantity influence*

It was observed an increase in the values of TOC (24.1 → 71.5%) along with the amount of catalyst (0.05 → 0.15 g), followed by a slight decline in the 69.8% (m = 0.20 g), due to limitations of diffusional that appear solid weight increases.

d) *Temperature influence*

Thus, the temperature range of 20-50 ° C, the average value of TOC was located around 36 ± 2% with a significant increase, 55.1%, but only reached at 60 ° C. Exceeding this temperature has reduced TOC values.

We note finally, the preliminary results of the re-use of spent catalyst **Co(2E2)-XC** (regeneration by pyrolysis at 750 ° C for 2 hours under an argon atmosphere) under the conditions shown in Figure 37 (T = 20 ° C; Q = 40 L / H, C0 = 100 mg / L; V = 25 ml m = 0.15 g catalyst; t = 180 min). The value of TOC obtained was of 32% (compared to 71.5%). This reduction can be attributed to severe leaching of metal from the catalyst or modifying the structure of the catalyst matrix.

III.5.3.2. *The comparative study of the efficiency of the catalytic carbon xerogel samples doped with transition metals in the CWAO of phenol*

The study was performed in a thermostated reactor, a semi-continuous, with stirring, operating at atmospheric pressure. Experiments were performed using 25 mL of phenol concentration 100 mg / L, 0.1 g of the catalyst (d <250 μm) at 25 ° C at an air flow rate of 40 L / hr and a reaction time of 180 min . For comparative purposes, has been carried out and wet air oxidation without catalyst, (WAO - Wet Air Oxidation) and in the presence of the blank sample, ie CWAO / K-XC in the same conditions as above.

Based on experimental data, the following hierarchy in catalysts efficiency could achieve Me (E2) –XC: Co (2E2) -XC> Co (1E2) -XC ≅ Ce(E2) -XC> Ni (E2) -XC> K-XC. Low TOC value in the use of K-XC, 3.3%, retention can be attributed to the adsorption of phenol on the surface of the carbon xerogel.

Regarding the preparation method the cation exchange depending on the solvent used (Table 8) of the samples Me-XC (role later CWAO-catalytic) were able to observe some relevant aspects, for example in the case of samples Ni-XC. Although the side to the Ni (A3) -XC (48.6%) was higher than that obtained in the case of Ni (E3) -XC (40.3%) could appreciate that the cation exchange process, in triplicates, held by -a similar mechanism (ethanol vs. double distilled water). On the contrary, if the Ni (E2) -XC (TOC 16.1%) and Ni (A2) -XC (TOC 34.3%) obtained in duplicate cation exchange, increasing the value of TOC was, as stated, more material. Overall observed positive influence not only double distilled water use vs. Ethanol in the cation exchange but that the fund expected growth in the number of shifts for the 2 vs. 3. The above observations have been validated in the case of Co-XC catalysts.

Indeed, comparing the Co (2E2) -XC (TOC 54.1%) and Co (A2) -XC (TOC 59.5%) catalysts we could re-confirm the superiority of cation exchange, ie, two shifts, if water bidistilled opposite ethanol direct influence on catalytic efficiency.

Further, from the comparison of the catalytic efficiency of the samples Co (1E2) -XC [COT 54.1%, the precursor Co (NO3) 2 • 6H2O] and Co (2E2) -XC [COT 36.3%, the precursor Co (CH3COO) 2 • 6H2O] prepared under identical conditions resulted in the beneficial influence of the existence, as counterion, to the nitrate nitrogen (NO3) compared acetate (CH3 COO-) in the cation exchange process.

CWAO value of TOC in the phenol in the presence of catalytic carbon aerogel sample of Co (A3) -AC was 68.8% and that of substantially close Co (A3) -XC, 67.5%. Since both samples were prepared under the same conditions of cation exchange (Table 8), the use of metal-doped carbon aerogel, Co (A3) -AC in the CWAO of phenol, there was non-sustainable, the more expensive the preparation of , ie, due to the need drying under supercritical conditions.

In conclusion of the above, the most effective method for the preparation of Me-XC was the one that was used as a precursor, nitrate metal cation, double distilled water as the solvent and the number of shifts of the solution of the metal cation, 3 (Table 8) .

As, in the end, the catalytic efficiencies of the samples Me (A3) -XC was examined as comparative. It was thus conducted the following hierarchy of decreasing catalytic efficiencies of the samples Me (A3) –XC: Co (A3) -XC> Ce (A3) -XC> Fe (A3) -XC> Ni (A3) -XC> Zn (A3) -XC.

III.5.4. Conclusions

Carbon xerogel doped by metals samples (Ce^{3+}, Co^{2+}, Fe^{3+}, Zn^{2+} and Ni^{2+}), Me-XC, produced by the sol-gel for the polycondensation reaction of the potassium salt of 2,4-dihydroxybenzoic acid with formaldehyde in the presence of K_2CO_3 and then cation exchange, were tested as catalysts in the catalytic wet air oxidation (CWAO) of phenol in aqueous solution.

By comparing the catalytic efficiencies of the samples Me-TOC values XC prepared by different types of cation exchange, ie, Ni-XC series vs. Co-XC series, and the maximum TOC values were observed in cases using double-distilled Water (A) as solvent, and 3 changes of fresh solution of the metal cation (A3).

Me-XC samples were characterized by SEM-EDX, TEM, XRD, FTIR and S_{BET}. These analyzes showed that the samples Me-XC are monolithic materials with large specific surface and a good dispersion of the metal nanoparticle. Me-XC hysteresis were of type IV, according to a mesoporous structure, while the pore size distribution was Gaussian one with a maximum pore diameter of 5 nm, specific surface area in the range of 115-275 m 2 / g, specific pore volume in the range of 0112-0190 cm 3 / g.

Maximum TOC values were observed for the samples, Co-XC 67.5% [Co (A3) -XC the conditions: T = 20 ° C; Q = 40 L / h; C0 = 100 mg / L; V = 25 ml; m = 0.10 g catalyst; t = 180 min] and 71.5% [Co (2E2) -XC the conditions: T = 20 ° C; Q = 40 L / h; C0 = 100 mg / L; V = 25 ml; m = 0.15 g catalyst; t = 180 min, Figure 41). If selected experiments in the absence of catalyst (WAO) or in the presence of a blank K-XC (CWAO), the oxidation reaction has not occurred (TOC <3.5%).

The results from the reuse of the Co(2E2)-XC catalyst showed that after its regeneration, the yield of the oxidation process of phenol decreased by approx. 55%, under the same reaction conditions, probably due to leaching from the matrix metal or the change in the XC catalyst.

It has been shown that metal-doped carbon xerogel can be successfully used as a catalyst in the catalytic wet air oxidation of phenol in aqueous solution.

III.6. CWAO OF PHENOL: REACTION PATHWAY AND KINETICS ANALYSIS

At the end of the efficacy CWAO studies the catalytic material it seemed interesting for comparative investigation by means of HPLC, by selecting the sample in terms of catalytic performance of each of the three classes discussed Me-TVZ, Me-D and Me-XC. These were: Cu(c1)-TVZ, Fe(c)-D and Co(A3)-XC.

Intermediaries of CWAO process of phenol is already well documented by other authors (Santos et al., 2002; Wu et al., 2003; Zhao et al., 2010) but with other catalysts, the discussion in this section will be limited commenting on the basic issues regarding our results in catalysts above.

III.6.1. HPLC monitoring

a) *Apparatus*

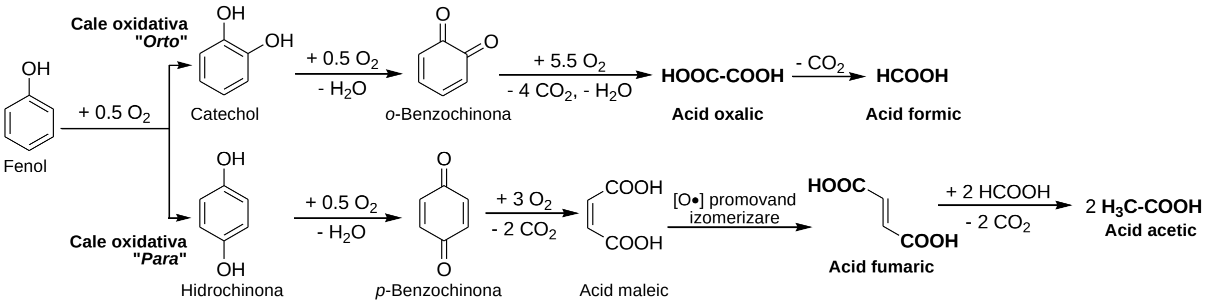
In order to examine the CWAO phenol oxidative decomposition as formation of intermediates and final products, reaction mixture samples (collected each 30 min.) were analyzed by means of a High Performance Liquid Chromatography (HPLC) Agilent 1200 instrument equipped with a DAD detector. A reverse phase C-18 (Nucleosil 100-C18, 250 mm × 4.5μm, Phenomenex) was used as the stationary phase. The separation of analytes on HPLC was conducted on a RPC18 column (mobile phase water-acetonitrile-phosphoric acid (89.9:10:01, v/v/v) at a column temperature of 25°C and a flow rate of 0.8 mL/min. The injection volume was 10 μL. The detection of the analytes was made by measuring the UV-absorption with the DAD detector at λ = 210, 230 and 254 nm.

III.6.2. Comparative results

Since **Fe-D**, **Cu-Z** and **Co-CX** catalysts exhibited the highest CWAO efficiencies, they were further considered for the study of the reaction pathways.

The radical (homolitic) nature of the mechanism in the case of phenol CWAO process is already well documented (Santos Yuste, 2002; Wu et al., 2003; Zhao et al., 2012). Therefore, we adopted the discussion of our results limited to some basic observation only. Regardless the catalyst used, merely phenol mineralization occurred during the first 30 min of the process. No oxidation organic compound was HPLC detected during this period, meanwhile the decreasing of phenol concentration was, however, different, ~39% on **Co-CX**, ~28% on **Fe-D** and ~25% on **Cu(b)-Z**. The total decrease of the phenol concentration through the whole oxidation time was ~86% on **Co-CX** and ~64% on both **Fe-D** and **Cu(b)-Z** catalysts.

Small traces of oxalic, formic, fumaric and acetic acid were identified after 30 min. Therefore, in agreement with the literature data, the proposed oxidation pathway was imparted into two major directions, "*Ortho* (or *Para*)-oxidation pathway" (Scheme 7). Just in the final stages the two directions interfered when, classically, formic acid was seen as a reduction agent against fumaric acid to produce acetic acid, which was dominant versus oxalic acid in all situations.



Schema 7. Proposed oxidation pathway in the presence of **Cu(c1)-TVZ**, **Fe(c)-D** şi **Co(A3)-XC**

III.6.3. CWAO of phenol: kinetics analysis

The title investigation was achieved in order to determine the catalytic reaction rate constants (k_{cat}), calculated by integrating the rate law in straight-line form, for a *pseudo* first-order kinetic model (k_{obs}). Indeed, due to the high air flows used (20-40 L/h), we assumed a constant concentration of the dissolved oxygen in the aqueous reaction mixture, according to its solubility: 5 mg/L (at 60°C) and 9 mg/L (at 20°C). In Figure 10, the corresponding plots for the CWAO of phenol using **Fe-D, Cu(b)-Z** and **Co-CX** catalysts are presented. The kinetic parameters thus deduced are collected in Table 15.

The linear plots (Figure 10) and their corresponding kinetic parameters (Table 15) validated the CWAO of phenol as a *pseudo* first-order catalytic process by i) R^2 correlation coefficients close to the unit and ii) k_{cat} values within the precision limits as ±5.1% for **Fe-D**, ±3.5% for **Cu(b)-Z**, however ±22% for **Co-CX**. The errors in the case of $\ln(C_0)_{calc}$ parameter against $\ln(C_0)_{exp}$ were less than 10% account being taken on the $\ln(C_0)_{calc}$ accuracy determination, ±0.3-5.5%.

Table 15. Pseudo first-order kinetic parameters for the CWAO of phenol using **Fe-D**, **Cu(b)-Z** and **Co-CX** as catalysts.

Catalyst	Initial concentration of phenol (C_0) at $t = 0$				Pseudo first-order kinetic model $\ln C_t = -k_{obs}t + C_0$ $k_{cat} = k_{obs} / C_{cat}$	
	$(C_0)_{exp}$ (mg/L)	$\ln(C_0)_{exp}$	$\ln(C_0)_{calc}$	Error* (%)	k_{cat}** (L/min·g)	R^2/n***
Fe-D	1000	6.9078	6.6335±0.0212	3.97	$(0.0473\pm0.0024)\cdot10^{-3}$	0.0812
Cu(b)-Z	1000	6.9078	6.7069±0.0193	2.91	$(0.0605\pm0.0021)\cdot10^{-3}$	0.0823
Co-CX	100	4.6052	4.0420±0.2210	8.82	$(1.4183\pm0.3150)\cdot10^{-3}$	0.1392

*Calculated as: $\{[\ln(C_0)_{exp} - \ln(C_0)_{calc}]/ \ln(C_0)_{exp}\}\times100$

C_{cat} as: 40 g/L [Fe-D** and **Cu(b)-Z**], 6 g/L (**Co-CX**)

***Number of points according to Figure 10

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SCIENTIFIC ACTIVITY

I. ISI articles

1. "*Novel metal modified diatomite, zeolite and carbon xerogel catalysts for mild conditions wet air oxidation of phenol: Characterization, efficiency and reaction pathway*"
Raluca Pleşa Chicinaş, Emese Gál, Horea Bedelean, Mircea Darabantu, Andrada Măicăneanu
Separation and Purification Technology, **2018**; 197: 36–46.
https://doi.org/10.1016/j.seppur.2017.12.050 (ISI 2016/2017: 3.359)

2. "*Ability of a montmorillonitic clay to interact with cationic and anionic dyes in aqueous solutions*"
R. Pleşa Chicinaş¸ H. Bedelean, R. Ştefan, A. Măicăneanu
Journal of Molecular Structure, **2018**; 1154: 187–195.
https://doi.org/10.1016/j.molstruc.2017.10.038 (ISI 2016/2017: 1.753)

3. "*Preparation, characterization, and testing of metal-doped carbon xerogels as catalysts for phenol CWAO*"
Raluca Pleşa Chicinaş, L. Cosmin Cotet, Andrada Măicăneanu, Mihai Vasilescu, Adriana Vulpoi *Environmental Science and Pollution Research*, **2017**; 24: 2980–2986.
https://doi.org/10.1007/s11356-016-8073-3 (ISI 2016/2017: 2.741)

4. "*Romanian (Măcicaş) zeolitic volcanic tuff for malachite green removal*"
Raluca Pleşa Chicinaş, Horea Bedelean, Andrada Măicăneanu
Studia UBB Chemia, LXI, **2016**; 4: 243-254. (ISI 2016: 0.244)

5. "*Characterization of Romanian bentonitic clays for the removal of dyes from wastewater*"
Raluca Pleşa Chicinaş, Adriana Tănase, Horea Bedelean, Andrada Măicăneanu
Analytical Letters, **2016**; 49: 2686-2701.
https://doi.org/10.1080/00032719.2015.1116004 (ISI 2016/2017: 1.15)

6. "*Catalytic wet air oxidation of phenol using metal modified zeolitic volcanic tuffs*"
Raluca Pleşa Chicinaş, Zoltán Zsebe, Horea Bedelean, Mircea Darabantu, Andrada Măicăneanu, , *Studia UBB Chemia*, LX, **2015**; 3: 237-246. (ISI 2015: 0.148)

II.International and national conferences

1. Sanda A. Măicăneanu, **Raluca Pleşa Chicinaş**, Emese Gal, Horea Bedelean, Mircea Darabantu, METALS MODIFIED DIATOMITE, ZEOLITE AND CARBON XEROGEL AS CATALYSTS FOR CATALYTIC WET AIR OXIDATION OF PHENOL: CHARACTERIZATION, OXIDATION EFFICIENCY AND REACTION PATHWAY, Advances in Chemical Oxidation for

Water & Wastewater Treatment Systems, ACS Fall National Meeting, Washington DC, **20-24 August 2017.**

2. **Raluca Pleşa Chicinaş,** Horea Bedelean, Andrada Măicăneanu, Anica Grigore, MATERIALE NATURALE FOLOSITE ÎN ELIMINAREA COLORANȚILOR DIN APELE UZATE, Sesiunea științifică anuală „Ion Popescu Voitești”, Departamentul de Geologie al Universităţii „Babeș-Bolyai”, Cluj-Napoca, România, **9 Decembrie 2016.**
3. **RC Pleşa Chicinaş,** A Tănase, H Bedelean, A Măicăneanu, VALORIZATION OF ROMANIAN CLAY MINERALS AS ADSORBENTS FOR DYES REMOVAL FROM WASTEWATERS, 10th International Processes in Isotopes and Molecules, Cluj-Napoca, România, **23-25 Septembrie 2015.**
4. **R. Pleşa Chicinaş,** A. Tănase, H. Bedelean, A. Măicăneanu, REMOVAL OF CATIONIC AND ANIONIC DYES FROM AQUEOUS SOLUTIONS USING RAW AND MODIFIED BENTONITE, Romanian International Conference on Chemistry and Chemical Engineering, Sibiu, România, **2-5 Septembrie 2015.**
5. Zsebe Z., **Pleşa Chicinaş R.C.,** Măicăneanu A., Cu-ZVT AS CATALYST FOR PHENOL WET AIR OXIDATION, International Conference Students for Students, Cluj-Napoca, Romania, **22-26 Aprilie 2015.**
6. **R.C. Pleşa Chicinaş,** L.C. Coteţ, A. Măicăneanu, PHENOL REMOVAL FROM WASTEWATERS USING Ce, Ni AND Co DOPED CARBON XEROGEL, 2nd International Conference on Chemical Engineering, Iasi, Romania, **5-8 Noiembrie 2014.**
7. **RC Pleşa Chicinaş,** A Maicaneanu, THE INFLUENCE OF REACTION PARAMETERS ON THE CATALYTIC WET AIR OXIDATION OF PHENOL, ELSEDIMA International Conference, Cluj-Napoca, Romania, **18-19 Septembrie 2014.**

III. Other scientific activities

Research internship in the period 01.07.2015 - 31.07.2015, under the direction of Prof. Dr. Andreas Lüttge from Marum, University of Bremen, Bremen, Germany.