Synthesis of ZnO/Fe₂O₃ Composite from Different Source of ZnO and its Use in Degradation of Methylene Blue

KhuloodAbed AL-Saade¹, HamzaHatem AL-Taie²

Department of Chemistry, College of Science, University of Baghdad(Iraq)

Abstract: The purpose of this research is to prepare and compare the ZnO composite/Fe₂O₃ which prepared from different sources(normalZnO, ZnO as waste from shaheed factory of copper and brass industry, nanoZnO)and their impact on the degrade of pollution as an example(methylene blue dye) in the aqueous solution with presence of UV irradiation and H_2O_2 as a Fenton's reaction at different temperature and dye concentration. The different products of ZnO/Fe₂O₃ composite was prepared by precipitation method, and the threecomposites were identify by AFM(Atomic Force Microscope) to find out the particle size and scan its morphology.

Keywords: NanoZnO, AFM, ZnO/Fe2O3 composite, methylene blue, Fenton's reaction

1. Introduction

Photocatalysis using semiconductor oxides have been used to solve pollution problems, and its proves to be effective degradation of great number of contaminants[1].ZnO appears to be a suitable alternative to TiO₂ since its photodegradation mechanism has been proven to be similar to that of TiO_2 . ZnO has been reported, sometimes, to be more efficient than TiO₂[2]. In heterogeneous photocatalysis system, when a suspension of a particular semiconductor is irradiated with a natural or artificial light, with an energy equals to or larger than the band gap, the electrons will be promoted to the conduction band (C.B.), leaving positive holes in the valence band (V.B.). If the electrons and holes are in a reaction, a steady state will be reached when the removal of electrons and holes equal the rate of generation illumination[3-5] Zinc oxide is an excellent hv photocatalytic oxidation material. It has been widely used to deal with wastewater, such as pharmacy wastewater, printing and dyeing wastes, papermaking wastewater[6].

Zinc oxide (ZnO) Nanoparticles are low cost and can be produced widely[7].

ZnO having lot of desirable properties such as high electron mobility, wider band gab, and exhibits luminescence at room temperature. The wide band gab of 3.3ev find use in varied application such as electronic device, bio medical field and sensor field [8]

(AOP)" are promising technologies which can be used todecolorization and mineralization to many kinds of dyes and transform dyes into biodegradable orharmless products" [9]. The Photo Fenton's oxidation "is a homogeneous catalytic oxidation process using a mixture of ferrous ionsand hydrogen peroxide" .Byusingartificial light or UV into Fenton's process lead to accelerate dve decolorizationand formation of (•OH) radicals. The main reactions in the photo-Fenton process for the formation of (•OH) radical includephoto reduction of ferric ion &photolysis of hydrogen peroxide, this processes shows in following equations respectively [10].

$$Fe^{+2} + H_2O_2 \xrightarrow{UV} Fe^{+3} + OH^-$$
 (1)

$$H_2O_2 \longrightarrow 2 \cdot OH$$
 (2)

$$Fe^{+3}+H_2O_2 \xrightarrow{UV} \bullet OH + Fe^{+2} + H^+$$
 (3)

A dye is a synthetic chemical compound used to transfer color to materials. Dyes are carbon based organic compounds, mostly include heavy toxic metals [11].

In the dye molecules, there are two important components : chromosphere which are responsible for producing the color; and auxochromes which reinforced the convergence of dye towards fiber[12-13]. At all events, the dyes used in the textile industry are basic dyes, acid dyes, reactive dyes, direct dyes, azo dyes, mordant dyes, vat dyes, disperse dyes, and sulfur dyes [14-16]. There are three types for dyes: firstly, cationic dyes, are widely used in acrylic, wool, nylon. These dyes include different chemical structures based on substituted aromatic group[17].Secondly, Anionic dyes, depend on a negative ion. They include many compounds from the most varied classes of dyes, which exhibit characteristic differences in structure (e.g., azoic, anthraquinone, nitro dyes) [18]. Thirdly, Nonionic dyes, are colorants with low water solubility that, in their disperse colloidal form, are suitable for dying and printing hydrophobic fibers and fabrics[19].

Methylene Blue or tetramethylthioninechloride $(C_{16}H_{18}N_3SCl)$ (MB) "is one of the high consuming materials in the dye industry and was selected as a model organic pollutant and its degradation was studied in the presence of Magnetite under UV" (Fig. 1). It behaviors as cationic thiazine dye with deep blue colorthat absorb @ 664 nm in the oxidized state while the reduced form of MB (i.e., leukomethylene blue-LMB) is colorless. In addition, MB has widely been used in environmental analysis such as wastewater discoloration [20]

Volume 6 Issue 10, October 2017 <u>www.ijsr.net</u> Licensed Under Creative Commons Attribution CC BY



2. Experimental Section

1) Determination of Maximum Adsprption (λ_{max}) :

Wavelength values utilize for estimation of quantity of compound are 664nm for Methylene blue

Figure 1: Chemical formula of methylene blue



Figure 2: UV-Visible absorption spectrum for Methylene blue dye

2) Calibration Curve



Figure 3: Calibration curve for methylene blue at $\lambda_{max} = 664 \text{ nm}, T=298 \text{K}$

3) Preparation of ZnO/Fe2O3 composite

The ZnO/Fe₂O₃ composite was prepared through the following steps: firstly, an aqueous dispersion of nomalZnO was prepared by adding 5g of normal ZnO to 250 mL H₂O under vigorous stirring for 3 h at 298 K. Secondly, sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate for 3h. Thirdly, 250 mL solution obtained from the second step was added drop by drop into the dispersion of ZnO prepared in the first step under vigorous stirring. Fourthly, the suspension was stirred for 3h followed by ageing at 100°C in an autoclave for 48h. Finally 500 ml of ZnO/Fe₂O₃composite suspension was obtained and ready for coating. Repeat the previous steps by using nanoZnO and shaheed ZnO (waste).

Stainless steel pipe with 4 cm diameter and 15 cm length figure (2) was supplied with copper coil surrounded the

outer cell surface and connected to the water bath for controlling the reactor solution temperature and lamp .

Inner cell surface firstly treated with concentrated HF acid to make the inner surface rough and able to pick up the coating, secondly the cell or photo react filled with ZnO/Fe₂O₃ Nanocomposite suspension for 10 minutes to allow forming stable coating layer, then the suspension evacuate from the reactor. To calcinated the catalyst ZnO/Fe₂O₃ layer, the photo reactor exposed to 500°C until the inner surface by compact with ZnO/Fe₂O₃ composite, by tested the transparency of distilled water when filled with it.



Figure 4: Complete system set up for photo degradation

3. Result and Discussion

1) Characterization of ZnO

Atomic Force Microscope:

The AFM analysis provides the measurements of average grain size (and the granularity cumulating distribution for both normal ZnO /Fe₂O₃ composite, ZnO Shaheed factory/Fe₂O₃ and nano ZnO /Fe₂O₃ composite. The average diameter is 122.85nm,107.72 nm and 73.08 nm for normal ZnO /Fe₂O₃ composite, shaheed factory ZnO /Fe₂O₃ and nano ZnO /Fe₂O₃ composite respectively



Figure 5: Atomic force microscope image for: A- normal ZnO /Fe₂O₃ composite, B- Shaheed factory ZnO /Fe₂O₃ ,CnanoZnO /Fe₂O₃ composite

2) Effect the H_2O_2 concentration in the Degradation process

Different H_2O_2 concentration were listed to investigate its effect on the M.B degradation percentage as show in table (1) and fig.6.

Volume 6 Issue 10, October 2017

<u>www.ijsr.net</u>

Licensed Under Creative Commons Attribution CC BY

Table 1: M.B percentage degradation by different ZnO/Fe₂O₃ composite using different H₂O₂ concentration

Cone M	% deg.	% deg.	% deg.
Conc./M	normal ZnO	Shaheed ZnO	Nano ZnO
0.0005	85.04	91.32	94.64
0.001	88.28	93.48	96.96
0.005	91.6	95.8	98
0.01	91.84	95.88	98.08
0.015	92.08	96.04	98.24
0.02	92.1	96.1	98.3

It is clear that the suitable H_2O_2 concentration in the degradation process is 0.005 M.



Figure 6: Variation of % deg. With H₂O₂ concentration for the three ZnO composite

Nano ZnO/Fe_2O_3 lead to the best %deg. and the %deg. increase with H_2O_2 concentration increasing.

3) Effect of ZnO sources on %deg. :

Percentage degradation (%deg.) was calculated from the following equation :

$$\% deg. = \frac{Co-Ce}{Co} * 100[21]$$
(4)

Where:

C₀: Initial concentration of Methylene blue

C_e: Concentration of Methylene blue after different radiation times.

Table (2) shows the variation of % deg. with time using the three types of prepared composites.

Table 2: %deg. for 25 ppm M.B at (different sources) ZnO/Fe₂O₃at 298K and 0.005M H₂O₂

	· · · 2 - J··· ·		2 - 2
t/min	%deg. Normal	%deg.	%deg. Nano
	ZnO	saheed ZnO	ZnO
10	79.1	84.6	85.4
20	82.5	86.8	87.6
30	85.8	92.4	93.2
40	88.1	93.7	96.1
50	90.1	94.4	97.2
60	91.6	95.8	98.0
70	91.7	95.9	98.1

It is clear that %deg. increase with time for all sources of ZnO but %deg. by nano ZnO>%deg. by shaheed ZnO> %deg. by normal ZnO dependent on average diameter for this compound shows in AFM.

Fig.7 shows the variation of %deg. with time for M.B by different ZnO sources.



Figure 7: Variation of % deg. with different sources of ZnO

Volume 6 Issue 10, October 2017

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

4) Effect of Temperature

The effect of temperature on the %deg. for the composites prepare from different sources of ZnO were listed in table 4 and fig 8.

Table 4: % deg. for 25 ppm M.B at (different sources)	ZnO
$/Fe_2O_3$ at time 70 min, and 0.005M H ₂ O ₂	

	2-5	,	- 2-2
T/K	%deg.	%deg.	%deg. nano
	normal ZnO	shaheed ZnO	ZnO
298	91.7	95.9	98.1
308	93.9	96.5	98.5
318	95.4	96.9	99.5
328	96.4	97.8	99.8

It is clear that increase %deg. with increase temperature for the three sources of ZnO and %deg. by nano> %deg. by shaheed> %deg. by normal.



Figure 8: Variation of M.B %deg. by the three ZnO composite at different temperature

5) Effect of the pH on % degradation of 25 ppm M.B in the presence of different ZnO composite and $H_2O_2(0.005M)$ and t= 60 min.

Table 5.and Fig.9 shows the effect of pH on %deg. by the different ZnO composite.

Table 9: % deg. of 25 ppm M.B by the three composite with different pH and 0.005 M H_2O_2

pН	%deg.	%deg.	%deg.
	normal ZnO	shaheedZnO	nanoZnO
3	71.2	79.2	82.6
4	79.2	85.0	88.9
5	88.0	90.3	95.3
6	89.9	93.9	96.9
7	91.6	95.8	98.0
8	90.4	92.9	94.4
9	89.0	91.0	93.1

The photodegradation reaction was also carried out under varying pH conditions from (3 to 9), by adjusting with HCl and NaOH [22], with ZnO kept at constant amounts of dye solutions (Fig. 9). The reaction was found to have low rates at neutral ranges of pH. While at higher and lower cases it was found to increase. This implies that alkaline as well as acidic conditions are favourable towards the formation of the reactive intermediates that is hydroxyl radicals is significantly enhanced, which further help in enhancing the reaction rate. On the other hand in neutral medium conditions the formation of reactive intermediates is relatively less favourable and hence less spontaneous.



Figure 9: Variation of %deg. of 25ppm M.B with different pH by the three ZnOcomposite and 0.005 M H₂O₂

Where:

6) Thermodynamic degradation study

The following first order equation were applied for the degradation of 25 ppm M.B and 0.005 M H_2O_2 by normal ZnO, shaheed ZnO and nanoZnO:

$$\operatorname{Ln} C_e = \operatorname{Ln} C_0 - kt \tag{5}$$

C₀: initial concentration of M.B

Ce: Concentration of M.B after exposing to UV at time t

Volume 6 Issue 10, October 2017

<u>www.ijsr.net</u>

Licensed Under Creative Commons Attribution CC BY

(8)

The Arrhenius equation is the following:					
$\mathbf{k} = \mathbf{A}\boldsymbol{e}^{-E\boldsymbol{a}/RT}[23]$	(6)				
$Lnk = Ln A - E_a/RT$	(7)				

Alternatively, the equation may be expressed as: $\mathbf{k} = \mathbf{A}e^{-Ea/kbT}$

where

- k is the rate constant.
- kb is the Boltzmann constant
- T is the absolute temperature (in kelvins)
- A is the pre- exponential factor
- E_a is the activation energy for the reaction (in K.J mol⁻¹)
- R is the universal gas constant.

Calculate the $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ from the following equations :

$A = KbT/h * e^{\Delta S \#/R} * e^{-\Delta H \#/RT}$ (9)

Table 6 and fig.10 represent the kinetic parameter for M.B degradation percentage by normal ZnO composite. **Table 6:** The Relationship between LnCe and t for 25ppm

Table 6: The Relationship between LnCe and t for 25ppm M.B , H_2O_2 (0.005M) and normal composite at different temperature

 $LnA=LnKbT/h+\Delta S^{\#}/R-\Delta H^{\#}/RT$

 $\Delta G^{\#}$ =-RT lnk

(10)

(11)

		1		
Time	Ln Ce	Ln Ce	Ln Ce	Ln Ce
(min)	(298K)	(308K)	(318K)	(328K)
10	1.77	1.64	1.38	1.31
20	1.59	1.37	0.78	0.74
30	1.33	1.24	0.61	0.53
40	0.80	0.70	0.47	0.44
50	0.73	0.57	0.40	0.30
60	0.69	0.65	0.16	0.01



Figure 11: The plot of: A- Ln k against 1/T, B- Ln A/T against 1/T for normalZnO composite

Fable 7:	The Therm	odynamic t	function	fornormalZnO	composite a	t 298K a	and 0.005N	$1 H_2O_2$
								2 - 2

T(K)	$K(min^{-1})$	Ln k	Ea(kJ.mol ⁻¹)	$A(S^{-1})$	Ln A/T	$1/T(K^{-1})$	$\Delta \hat{H}^{\#}(kJ.mol^{-1})$	$\Delta S^{\#}(kJ.mol^{-1}K^{-1})$	$\Delta G^{\#}(kJ.mol^{-1})$
298	0.021	-3.717			-8.079	0.0033			92.09
308	0.0225	-3.785	2716	0.0022	-8.112	0.0032			96.92
318	0.0227	-3.794	5./10	0,0925	-8.144	0.0031	-2.66	-0.205	100.30
328	0.0243	-3.863			-8.175	0.0030			105.34

Volume 6 Issue 10, October 2017

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

The energy of (E_a) was calculated from the slope of the plot. Therefore, otherparameters for thermodynamic such as entropy, free energy of activation & enthalpy were also evaluated. The positive energy of activation refer to the reaction is less energy intensive. This could be because the activated state is a good solvated structure formed between the dye molecules and the reaction intermediate that is hydroxyl radical which is also supported by positive entropy of activation.

The rate of reaction (k) increase with increase temperature . Therefore, the %deg. increase with increase temperature and helps to acceleration the velocity of both the dye molecules and hydroxyl radicals to interact to each other. The degradation of M.B dye with ZnO occur as the following equation :

Table 8 and fig.12 represent the kinetic parameter for M.B degradation percentage by shaheed factory ZnO composite.

Table 8: The Relationship between LnCe and t for 25ppm M.B, H_2O_2 (0.005M) and shaheed factory ZnO composite

T	11_2O_2 (0.005101) and shalleed factory ZhO con-								
	Time	Ln Ce	Ln Ce	Ln Ce	Ln Ce				
	(min)	(298K)	(308K)	(318K)	(328K)				
	10	1.62	1.62	1.20	1.01				
	20	1.43	1.26	0.53	0.50				
	30	0.90	0.83	0.49	0.44				
	40	0.64	0.49	0.28	0.21				
	50	0.53	0.40	0.16	0.09				
	60	0.44	0.35	0.02	-0.04				

Figure 12: The plot of LnCeagainst t/min for Shaheed factory ZnO composite

Table 9 and fig13 represent the thermodynamic function for M.B degradation percentage by shaheed factory ZnO composite.

Figure 13: The plot of : A- Ln k against 1/T, B- Ln A/T against 1/T for Shaheed factory ZnO composite

Volume 6 Issue 10, October 2017 <u>www.ijsr.net</u> <u>Licensed Under Creative Commons Attribution CC BY</u>

	Table 9: The Thermodynamic function for Shaheed factory ZnO composite at 298K and 0.005M H_2O_2								
T(K)	$K(min^{-1})$	Ln k	Ea(kJ.mol ⁻¹)	$A(S^{-1})$	Ln A/T	$1/T(K^{-1})$	$\Delta H^{\#}(kJ.mol^{-1})$	$\Delta S^{\#}(kJ.mol^{-1}K^{-1})$	$\Delta G^{\#}(kJ.mol^{-1})$
298	0.0191	-3.958			-8.350	0.0033			98.06
308	0.0196	-3.932			-8.383	0.0032	-2.66	-0.207	100.68
318	0.0199	-3.917			-8.415	0.0031			103.55
328	0.0217	-3.830	3.317	0.0704	-8.446	0.003			104.44

Table 10 and fig.14 represent the kinetic parameter for M.B degradation percentage by nanoZnO composite.

Table 10: The relationship between LnCe and t for 25ppm M.B , H_2O_2 (0.005M) and nanoZnOcomposite

Time	Ln Ce	Ln Ce	Ln Ce	Ln Ce
(min)	(298K)	(308K)	(318K)	(328K)
10	1.27	1.20	1.05	0.87
20	0.83	0.78	0.50	0.41
30	0.65	0.57	0.40	0.33
40	0.40	0.37	0.25	0.02
50	0.24	0.19	0.02	-0.06
60	0.14	0.13	-0.05	-0.16

Figure 14: The plot of LnCeagainst t/min for nanoZnO composite

Table 11and fig15 represent the thermodynamic function for M.B degradation percentage by nano ZnO composite.

Figure 15: The plot of: A- Ln k against 1/T, B- Ln A/T against 1/T for nanoZnO composite

Table 11: Show the thermody	ynamic function for Nano ZnO	composite at 298K, 0.005M H ₂ O ₂
-----------------------------	------------------------------	---

T(K)	$K(min^{-1})$	Ln k	Ea(kJ.mol ⁻¹)	$A(S^{-1})$	Ln A/T	$1/T(K^{-1})$	$\Delta H^{\#}(kJ.mol^{-1})$	$\Delta S^{\#}(kJ.mol^{-1}K^{-1})$	$\Delta G^{\#}(kJ.mol^{-1})$
298	0.0198	-3.922			-8.532	0.0033			97.17
308	0.0203	-3.897			-8.565	0.0032	-2.66	-0.209	99.79
318	0.0209	-3.869			-8.597	0.0031			102.29
328	0.0219	-3.821	2.751	0.0587	-8.628	0.003			104.19

Volume 6 Issue 10, October 2017

www.ijsr.net

Licensed Under Creative Commons Attribution CC BY

4. Conclusion

In this work ZnO/Fe_2O_3 composite were synthesized from different source of ZnO by precipitation method characterization of composite such as average diameter and morphology were achieved by AFM to compare between the three composites.

The average diameter were obtained for nanoZnO /Fe₂O₃ composite<shaheed factory ZnO/ Fe₂O₃ composite < normal ZnO/Fe₂O₃ composite, therefore the %deg. increase with decrease the average diameter and increase with increase temperature .In addition, this study refer to advantage of the shaheed ZnO and can be turned it to a useful compound in dye removal by introducing it in the preparation of composite based on comparing the AFM value before and after the composite preparation. E_a for: nano ZnO>shaheed ZnO> normal ZnO, therefore the degradation for nano composite is easily from shaheed composite and the latter is easily degradation from normal composite.

References

- Behnajady M. A, N. Modirshahla and R.Hamzavi, (2006). "Kinetic study on photocatalytic degradation of C.I.Acid Yellow23by ZnO photocatalyst ",*JHazard.Mater.B*, 133.
- [2] Daneshvar N.,D.Salari,A.R.Khataee, (2004)."Photocatalytic degradation of azo dye acid red14 in water on ZnO as an alternative catalyst to TiO2".J. Photochemistry and Photobiology A:Chemistry162.
- [3] Hurum,D.CA.G.Agrios,andA.Kimberly,
 (2003).GrayExplaining the Enhanced Photocatalytic Activity of Degussa P25 Mixed-Phase TiO2 Using EPR,J.Phys. Chem.B,107,.
- [4] Zhang
 M.,G.Sheng,J.Fu,T.An,X.Wang,X.Hu(2005)."Novelpre paration of nanosizedZnO–SnO2with high photocatalytic activity by homogeneous co-precipitation method". *Materials Letters* 59
- [5] Fujishima, A. K.Honda(1972). "Electrochemical photolysis of water at a semiconductor electrode". *Natur*,238.
- [6] Vora,S.KJ.J..Chauhan,K.C.Parmar,S.B.Vasava,S.Sharm a and L.S.Bhutadiy (2009). "Kinetic Study of Application of ZnOas a Photocatalyst in HeterogeneousMedium ".*E-Journal of Chemistry*, 6(2),.
- [7] Chen CC,Liu P, Lu CH(2008)." Synthesis and characterization of nano-sized ZnO powders by direct precipitation method". ChemEng J 144(3):509-513.
- [8] Hamid Reza Ghorbani, Ferdosparsamehr, Hosseinpazo, Brhradmosavar Rahmani. (2015)."Synthesis of ZnO nanoparticles by precipitation method". Oriental journal of chemistry.31(2),1219-1221
- [9] R. Andreozzi, V. Caprio, A. Insola, and R. Marotta, (1999). "Advanced oxidation pro-cesses (AOP) for water purification and recovery," *Catal. Today*, vol. 53, pp. 51–59.
- [10] H. J. H. Fenton, (1894) "Oxidation of tartaric acid in the presence of iron," *Chem. Soc. J. Lond.*, vol. 65, pp. 899-910.

- [11] Fraige, A.(2012). "Adsorption from aqueous solution onto natural and acid activated bentonite", American journal of environmental Science. 8(5): 510-522.
- [12] Sriniva San. A., T. Virargharan, (2012). "Decolorization of dye waste water by biosorbent: a review". J. Environ. Manage, 91 : 1915-1929.
- [13] Uygur, A. (1997). "An overview of oxidative and photo oxidative decolorization treatment of texlile wastewaters". J.Soc. Dterscolourists 113 (7/8): 211-217.
- [14] Mohamed, A.; Dalia K. ;Azlua, A.(2011)." Cationic and anionic dye adsorption by agricultural solid wastes: A comprehensive. Review". Desalination. 280, 1-13.
- [15] Wilcok, A. (1992). "Spectrometric analysis of electro chemically stimulated dispersed dye bath effluent". Text, Chem. Color. 24: 29-37.
- [16] Namit,T. (2013). "Cationic and anionic dye adsorption by agricultural solid waste: A comprehensive review". Journal of Applies Chemistry. 5: 19-108.
- [17] Devi, R.; Singh, V.;andKumer, A. (2008). "COD and BOD reduction from coffee processing wastewater using avocado peel carbon". J. Biores. Technol. 99: 1853-1860.
- [18] Vodivelan, V.; Kumar, K.V. (2005). "Equilibrium kinetic,mechanism, and process design for the sorption of methylene blue onto rice husk".J.Colloid. Interface. Sci. 286: 90-100.
- [19] Alkhafagy, J.; Kadhum. (1999). Industrial chemistry. Faculty of Education Ibn al-Haitham. University of Baghdad. Second Edition.
- [20] S. Pande, S. K. Ghosh, S. Nath, S. Praharaj, S. Jana, S. Panigrahi, S. Basu, and T. Pal. (2006). "Reduction of methylene blue by thiocyanate: Kinetic and thermodynamic aspects," *J. Colloid. Interf. Sci.*, vol. 299, pp.421-427.
- [21] A.Al-Kdasi, A. Idris, K. Said and C.T. Guan. (2004). "Treatment of textile wastewater by advanced oxidation process". Global Nest the Int. J. (6) 222-230.
- [22] Al-Bayati Y. K. and Aljabari F. I.,Synthesis of Ibuprofen-Molecularly Imprinted Polymers Used asSensors to Determine Drug in Pharmaceutical Preparations, Asian J. of Chemistry,2016, 28(6), 1376-1380.
- [23] Arrhenius, S.A. (1889). "Über die Dissociationswärme und den Einfluß der Temperatur auf den Dissociationsgrad der Elektrolyte".Z. Phys. Chem. 4: 96–116. doi:10.1515/zpch-1889-0108.