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Perspectives for Photocatalytic Decomposition of Environmental Pollutants and Pathogens on Photoactive Particles of Soil Minerals

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Abstract: The literature shows that both in laboratory and in industrial conditions, photocatalytic oxidation method copes quite well with the degradation of the most organic substances, including environmental toxins and molecular components of pathogenic microorganisms. However, the effective utilization of photocatalytic processes for environmental decontamination and disinfection require significant technological advancement both in the area of semiconductor material synthesis and its application. Here we focused on the presence and 'photocatalytic capability' of photocatalysts among soil minerals, and their potential contribution to the environmental decontamination *in vitro* and *in vivo*. (The issue is sketched from the perspective of chemists and environmental scientist.) Reactions caused by sunlight on the soil surface are involved in its normal redox activity. It appears that some of them may take part in the soil decontamination. However, their importance for decontamination *in vivo* cannot be overstated due to diversity of soils on the Earth caused by the environmental conditions, such as climate, parent material, relief, vegetation *etc*. The solar-light induced reactions are just a part of extremely complicated processes dependent on a plethora of environmental determinates. Such multiplicity of affecting factors, which we tried to sketch from the perspective of chemists and environmental scientist, makes us rather sceptical about the effectiveness of the photocatalytic processes *in vivo*. On the other hand, there is a huge potential of the soils as the alternative source of useful photocatalytic materials of unique properties.

Keywords: photocatalysis; semiconductors; solar light; soil minerals; micro-pollutants; pathogens; environmental decontamination

1. Introduction

The subject of relationships between pollution and infectious disease has become a hot topic among scientists even prior to the recent COVID-19 pandemic years [1]. The pandemic itself has sparked a surge in interest in implementing measures to eliminate toxins, viruses and other pathogens from the environment. Since the advent of the photocatalysis the method has been proposed for 'self-cleaning' solutions, maintenance of clean surfaces, and for depolluting applications allowing removal of inorganic and organic pollutants present in heavily polluted environments [2–5]. The decomposition and destruction of pollutants are caused by processes involving highly reactive oxidative species (ROSs) generated on the surface of semiconductors during visible and ultraviolet light irradiation [6–8].

For the record: The semiconductors are characterized by a filled valence band (VB) and an empty conduction band (CB) [9–11]. Thus, upon light-illumination by photons of energy higher than the band gap (E_{BG}) [12], electrons are excited and promoted into CB (e^-_{CB}), leaving a holes (h^+_{VB}) in VB. The photo-generated e^-_{CB} - h^+_{VB} pairs will then migrate to the surface of photocatalyst, where, in contact with the aqueous environment and oxygen, produce ROSs [8,13]. (A less topic oriented reader can easily find details, and in-depth knowledge on semiconductors and photocatalysis in many basic books and articles, including those published in the *Molecules* journal of which we will mention only a few [2–5,7–9,14–30]. The basic issues related to environmental pollution and related chemistry problems can be found in many textbooks and monographs [31–34].)

It is necessary to highlight here that four essential elements for photocatalytic oxidation should be present: (i) a photocatalyst, stable under given pH and temperature conditions, (ii) solar light, (iii) atmospheric oxygen, and (iv) humidity. Sufficiently small E_{BG} of photocatalyst allows absorption of natural solar light, whereas atmospheric oxygen and humidity allow the formation and transport of ROSs out of the photocatalyst surface.

The most common photocatalysts are represented by metal oxides or sulphides such as TiO_2, ZnO, ZnS, Fe_2O_3, and SnO_2, or less frequently used but intensively tested Fe_3O_4, MoS_2 and CdS [4,25,35–40]. The photocatalysts are natural or synthesized in laboratory conditions on a technical scale [41,42].

A plethora of experimental and theoretical works conducted other the last twenty years or so, demonstrate the effort put into improving the efficiency of photocatalysts. The effort on obtaining desired changes in the characteristics of photocatalytic usually goes in two directions: (ii) utilization of a broader light absorption spectrum for enhanced quantum-yield of ROS, and (iii) increase the reducing properties of e^-_{CB} , with the goal of being able to reduce water to the molecular hydrogen.

What is worth emphasizing, the manipulation of dimensions and shape of a semiconductor-particle allows the change of photocatalysts' characteristics [9,43–46]. Another popular and quite effective way to 'tune' E_{BG}, Fermi-level (*i.e.* reduction-potentials of e^-_{CB} and h^+_{VB}), the molar absorption coefficient (ε), and other characteristics of the material, is by the engineering that introduces dopants and other defects into the structure of the semiconductor [47–56]. Thus, under certain conditions, even high dielectric constant oxides like ZrO_2 can be utilized to build binary oxide photocatalysts [57–61].

Due to the incorporation of various 'impurity' elements and crystal lattice defects, when engineered $E_{BG} \leq$ *ca.* 3.3 eV (380 nm), these materials could possess the so called visible-light-driven photocatalytic activity (VLD) [62–64,50]. However, one can expect some disadvantages of extended defects, which could provoke the recombination of e^-_{CB} - h^+_{VB} -pair [21,49]. (Although it is unfavourable for photocatalysis, the enhanced e^-_{CB} - h^+_{VB} recombination may be desirable for other application of light-absorbing minerals. Since, for instance, the production of ROS is highly undesirable for the UV-filters ('sunscreens') [65–72].)

The particles of naturally occurring minerals have unique chemical composition that contains a main component and many other trace amounts of elements. They are formed through complex biogeochemical processes that are hardly understood, and, despite many attempts, very difficult to imitate in the laboratory conditions [73–78].

This directs interest to natural photoactive minerals, with their possible sources related to shallow deposits in the Earth's crust and in soil. In this review we focused on the presence of photocatalysts among minerals in the surface layers of the Earth's crust, and their potential contribution to the environmental decontamination *in vitro* and *in vivo*, examining the issues from the perspective of chemists and environmental scientist.

2. Redox Activity of Soil

Oxidation and reduction reactions occur instantly in soils. Soil redox abilities depend on the properties and concentration of substances contained in the so-called 'soil solution'. An indicator characterizing the oxidation and reduction ratios in soil is its reduction potential $\boldsymbol{E}_\mathbf{h}$, which can be calculated based on redox half-reactions with the Nernst equation [79–82]:

$$E_\mathrm{h} = E_\mathrm{h}^\ominus + 2.303\frac{RT}{nF}(\log\frac{\{\mathrm{Ox}\}}{\{\mathrm{Red}\}} + m \times \mathrm{pH}), \quad (1)$$

Where $E_\mathrm{h}^\ominus$ [V *vs* SHE] is the reduction potential under standard conditions (all activities = 1, P_{H_2} = 1 atm, $\{H^+\}$ = 1 M); $\boldsymbol{R}$ is universal gas constant [J mol^{-1} K^{-1}]; T is the temperature [K]; m is the number of exchanged protons; n is the number of exchanged electrons; F is Faraday constant [C mol^{-1}]; {Ox}/{Red} is the ratio of the activities of oxidized to reduced species.

In addition to $\boldsymbol{E}_\mathbf{h}$, in the 'soil chemistry', the reader may encounter two more indicators of soil redox activity, which are less known to general chemists, *i.e.* ***r*H** and **pe**. The redox potential of soil solutions depends on the degree of saturation with molecular hydrogen (H_2) and the pH of the environment. The higher H_2-concentration causes the greater reduction-capacity of the solution and *vice versa*). The ***r*H** indicator is a negative logarithm of the hydrogen pressure in the soil - 'soil solution' system, which demonstrates the relationship between redox and soil pH [83].

$$r\mathrm{H} \simeq \frac{E_\mathrm{h}}{30} + 2\mathrm{pH}, \quad (2)$$

Because many redox-active elements (mainly metals) are involved in soil redox processes, **pE** (or **pe**) equal to -log{activity of electron}, seems to be a more universal redox indicator [74,82,84,85].

$$\mathrm{pE} = \log K – \mathrm{pH}, \quad (3)$$

where $K = \{\mathrm{Red}\} / (\{\mathrm{Ox}\} \times \{e^-\}^n \times \{\mathrm{H_3O^+}\}^m)$.

In all systems, $\boldsymbol{E}_\mathbf{h}$, ***r*H**, and **pE** are governed by pH, and the activities of oxidized {Ox}, and reduced species {Red}. (For example, $\boldsymbol{E}_\mathbf{h}$ higher than 200 mV is usually associated with the dominance of electron acceptors in soil *e.g.* O_2, NO_3^-, MnO_2, Fe_2O_3.) For complex systems such as soil, the coverage of all components in the equations can be extremely complicated, but it is solvable thanks to the professional geochemical software [86,87].

Normal limits of pH in the environment are 4-9, lower are found in acid sulfate soils, while the upper end of the pH limits is associated with water in contact with carbonate rocks. Whereas, theoretical limits of $\boldsymbol{E}_\mathbf{h}$ are determined by water instability and release of gases, O_2 upon oxidation, and H_2 upon reduction. The upper limit of $\boldsymbol{E}_\mathbf{h}$ is defined by the oxidation of H_2O ($2\mathrm{H_2O} \rightleftharpoons \mathrm{O_2} + 4\mathrm{H^+} + 4\mathrm{e^-}, E^\ominus = 1.23$ V), whereas, the its lower limit is defined by the reduction of H^+ ($\mathrm{H_2} \rightleftharpoons 2\mathrm{H^+} + 2\mathrm{e^-}, E^\ominus = 0.00$ V). The potentials of above half-reaction depend on the pH and follow the Nernstian equations. (Importantly, major photoactive minerals (see bellow) remain stable in this pH and E_h ranges [74,79,82,88].)

From an agricultural point of view, $\boldsymbol{E}_\mathbf{h}$ values within 200-750 mV are beneficial for normal plant development. The $\boldsymbol{E}_\mathbf{h}$ value of 750 mV for soil, is associated with full aerobiosis, at which there is already a violation of the correctness in plant nutrition, while $\boldsymbol{E}_\mathbf{h}$ lower than 200 mV is associated with reducing processes harmful for plants. The potential $\boldsymbol{E}_\mathbf{h}$ is mainly influenced by soil moisture, pH and microbiological reactions. Increasing soil moisture reduces the value of $\boldsymbol{E}_\mathbf{h}$, drying has the opposite effect. $\boldsymbol{E}_\mathbf{h}$ fluctuates depending on hydrologic regimes [89] and the season. For instance, in the temperate climate zone (of middle latitudes 23.5° to 66.5° N/S of Equator) is the lowest in spring, increases in summer and autumn [83].

It seems obvious that sunlight has its share of daily and seasonal fluctuations of $\boldsymbol{E}_\mathbf{h}$, since the photochemical redox processes occur upon sunlight illumination. Interestingly, even the effects of soil drying by sunlight are different from those by drying in the dark [74]. Although, light will generally not penetrate the soil surface deeper than 2 mm but, on light-exposed soil, this depth will be sufficient to create a redox interface, especially since upward diffusion may extend the effective depth of sunlight. The redox balance in soil is affected by exposure to sunlight. Numerous soil components are photoactive, and their chemistry will vary significantly in sunlight compared to darkness. They include Fe(III) species, polycarboxylates, humic acids, and MnO_2. Probably the most prevalent reactions in soil are photoredox transformations of Fe(III) and associated organic ligands [90–92].

The balance of redox in soil changes under the influence of light in numerous, often competing processes. These may be reversible processes such as the Fe^{2+}/Fe^{3+} redox transformations, as well as irreversible, after which reaction products such as CO_2 leave the soil environment. Importantly, environmental toxins may also participate in photochemical processes, which may lead to their degradation. As examples, they are often cited degradation of aromatic and polyaromatic hydrocarbons, aryl ketones and dioxins caused by the $^{\bullet}OH$-radicals produced in the Haber-Weiss reaction between Fe^{2+} and H_2O_2 [74,93], and photocatalytic nitrogen-oxide conversion in red soil [94,95].

3. Photoactalytic Activity of Earth's Lithosphere Minerals. Natural Semiconductors Present in the Crust

The semiconducting minerals are ubiquitous on Earth, most of which are common mineral phases located near the Earth’s surface: oxides [*e.g.*, *rutile* (TiO_2), *limonite* ($FeTiO_3$), *hematite* (Fe_2O_3), *goethite* ($FeOOH$)] and sulphides [*e.g.*, *sphalerite* (ZnS), *greenockite* (CdS), *pyrite* (FeS_2)] [85]. Xu and Schoonen have reviewed about fifty kinds of semiconducting metal oxides and sulphide minerals, as shown in Table 1 [26]. (Importantly, the existence of the *common name* indicates the occurrence of mineral in nature.)

Table 1. The E_{BG}, $E^{\ominus}_{VB}$, $E^{\ominus}_{CB}$ energy positions at the zero point of charge (pH_{zpc}) for oxides and sulphides base on the Xu and Schoonen [26] data. The $E^{\ominus}_{VB}$ and $E^{\ominus}_{CB}$ values are recalculated to the electrochemical scale $E(vs\ SHE)=-E(AVS)-4.44$ V [96,97].

Mineral / oxide	E_{BG} **/eV (nm)**	$E^{\ominus}_{VB}$ **/V**	$E^{\ominus}_{CB}$ **/V**	pH_{zpc}	**Mineral / sulphide**	E_{BG} **/eV (nm)**	$E^{\ominus}_{VB}$ **/V**	$E^{\ominus}_{CB}$ **/V**	pH_{zpc}
Ag_2O	0	0.25	0.25	11.2	Ag_2S (*Argentite*)	0.92 (1348)	1.02	0.06	2
$AlTiO_3$	3.6 (345)	2.8	-0.8	8.23	$AgAsS_2$ (*Trechmannite*)	1.95 (635)	2.02	0.07	2
$BaTiO_3$	3.3 (375)	3.44	0.14	9	$AgSbS_2$ (*Miargyrite*)	0	0.07	0.07	2
Bi_2O_3 (*Bismite*)	2.8 (443)	3.19	0.39	6.2	As_2S_3 (*Orpiment*)	2.5 (496)	2.64	0.14	2
CdO (*Monteponite*)	2.2 (564)	2.37	0.17	11.6	CdS (*Greenockite*)	2.4 (517)	2.26	-0.46	2
$CdFe_2O_4$	2.3 (539)	2.54	0.24	7.22	Ce_2S_3	0	-0.85	-0.85	2
Ce_2O_3	2.4 (517)	1.96	-0.44	8.85	CoS	0	0.73	0.73	2
CoO	2.6 (477)	2.55	-0.05	7.59	CoS_2 (*Catterite*)	0	1.05	1.05	1.5
$CoTiO_3$	2.25 (551)	2.45	0.2	7.41	$CoAsS$ (*Cobaltite*)	0	0.52	0.52	2
Cr_2O_3 (*Eskolaite*)	3.5 (554)	2.99	-0.51	8.1	CuS (*Covellite*)	0	0.83	0.83	2
CuO (*Tenorite*)	1.7 (729)	2.22	0.52	9.5	Cu_2S (*Chalcocite*)	1.1 (1127)	1.1	0	2
Cu_2O (*Cuprite*)	2.2 (564)	1.98	-0.22	8.53	CuS_2 (*Villamaninite*)	0	1.13	1.13	2
$CuTiO_3$	2.99 (415)	2.87	-0.12	7.29	Cu_3AsS_4 (*Enargite*)	1.28 (969)	1.59	0.31	2
FeO (*Wustite*)	2.4 (517)	2.29	-0.11	8	$CuFeS_2$ (*Chalcopyrite*)	0.35 (3542)	0.88	0.53	1.8
Fe_2O_3 (*Hematite*)	2.2 (564)	2.54	0.34	8.6	Cu_5FeS_4 (*Bornite*)	0	0.11	0.11	2
Fe_3O_4 (*Magnetite*)	0.1 (12398)	1.39	1.29	6.5	$CuInS_2$	1.5 (827)	2.62	-0.38	2
$FeOOH$ (*Goethite*)	2.6 (477)	3.24	0.64	9.7	$CuIn_5S_8$	1.26 (984)	0.91	-0.35	2
$FeTiO_3$ (*Ilmenite*)	2.8 (443)	2.65	-0.15	6.3	Dy_2S_3	2.85 (435)	1.77	-1.08	2
Ga_2O_3 (*β-Ga_2O_3*)	4.8 (258)	3.31	-1.49	8.47	FeS (*Pyrrhotite*)	0.1 (12398)	0.63	0.53	3
HgO (*Montroydite*)	1.9 (653)	2.59	0.69	7.3	FeS_2 (*Pyrite*)	0.95 (1305)	1.43	0.48	1.4
$Hg_2Nb_2O_7$	1.8 (689)	2.67	0.87	6.25	Fe_3S_4 (*Greigite*)	0	0.74	0.74	2
$Hg_2Ta_2O_7$	1.8 (689)	2.7	0.9	6.17	$FeAsS$ (*Arsenopyrite*)	0	0.57	0.57	1.5

In_2O_3 (*India*)	2.8 (443)	2.24	-0.56	8.64	Gd_2S_3	2.55 (486)	1.68	-0.87	2
$KNbO_3$	3.3 (376)	2.5	-0.8	8.62	HfS_2	1.13 (1097)	1.4	0.27	2
$KTaO_3$	3.5 (354)	2.63	-0.87	8.55	HgS (*Cinnabarite*)	0	0.08	0.08	2
La_2O_3	5.5 (225)	3.59	-1.91	10.4	$HgSb_4S_8$	1.68 (738)	2.05	0.37	2
$LaTi_2O_7$	0	-0.54	-0.54	7.06	In_2S_3	0	-0.74	-0.74	2
$LiNbO_3$	3.5 (354)	2.83	-0.67	8.02	La_2S_3	0	-1.19	-1.19	2
$LiTaO_3$	0	-0.89	-0.89	7.94	MnS (*Alabandite*)	3 (413)	1.87	-1.13	2
$MgTiO_3$ (*Geikielite*)	3.7 (335)	3.01	-0.69	7.81	MnS_2 (*Hauerite*)	0	0.55	0.55	2
MnO (*Manganosite*)	3.6 (345)	2.65	-0.95	8.61	MoS_2 (*Molybdenite*)	1.17 (1060)	1.46	0.29	2
MnO_2 (*Pyrolusite*)	0.25 (4959)	1.64	1.39	4.6	Nd_2S_3	2.7 (459)	1.56	-1.14	2
$MnTiO_3$	0	-0.4	-0.4	7.83	NiS (*Polydymite*)	0	0.59	0.59	2
Nb_2O_5 (*Niobia*)	3.4 (367)	3.55	0.15	6.06	NiS_2 (*Vaesite*)	0	0.95	0.95	0.6
Nd_2O_3	4.7 (264)	3.13	-1.57	8.81	OsS_2 (*Erlichmanite*)	0	0.3	0.3	2
NiO (*Bunsenite*)	3.5 (354)	3.06	-0.44	10.3	PbS (*Galena*)	0.37 (3351)	3.37	0.3	1.4
$NiTiO_3$	2.18 (569)	2.44	0.26	7.34	$Pb_{10}Ag_3Sb_{11}S_{28}$	1.39 (982)	1.54	0.15	2
PbO (*Massicot*)	2.8 (443)	2.38	-0.42	8.29	$Pb_2As_2S_5$	1.39 (982)	1.66	0.27	2
$PbFe_{12}O_{19}$	2.3 (539)	2.56	0.26	7.17	$PbCuSbS_3$	1.23 (1008)	1.4	0.17	2
PdO	0	0.85	0.85	7.34	$Pb_5Sn_3Sb_2S_{14}$	0.65 (1907)	1.16	0.51	2
Pr_2O_3	3.9 (318)	2.7	-1.2	8.87	Pr_2S_3	2.4 (517)	1.39	-1.01	2
Sb_2O_3 (*Valentinite*)	3 (413)	3.38	0.38	5.98	PtS_2	0.95 (1305)	2.04	1.09	2
Sm_2O_3	4.4 (282)	3.03	-1.37	8.69	Rh_2S_3	1.5 (827)	1.67	0.17	2
SnO (*Romarchite*)	4.2 (295)	3.35	-0.85	7.59	RuS_2 (*Laurite*)	1.38 (898)	1.83	0.45	2
SnO_2 (*Cassiterite*)	3.5 (354)	3.56	0.06	4.3	Sb_2S_3 (*Antimonite*)	1.72 (721)	2	0.28	2
$SrTiO_3$ (*Tausonite*)	3.4 (365)	2.2	-1.2	8.6	Sm_2S_3	2.6 (477)	1.55	-1.05	2
Ta_2O_5 (*Tantite*)	0	-0.11	-0.11	2.9	SnS (*Herzenbergite*)	1.01 (1228)	1.23	0.22	2
Tb_2O_3	3.8 (326)	2.8	-1	8.5	SnS_2 (*Berndtite*)	0	0	0	2
TiO_2 (*Anatase*)	3.2 (387)	2.97	-0.23	5.8	Tb_2S_3	2.5 (496)	1.57	-0.93	2
Tl_2O_3 (*Avicennite*)	1.6 (775)	1.71	0.11	8.47	TiS_2	0	0.32	0.32	2
V_2O_5 (*Karelianite*)	2.8 (443)	3.05	0.26	6.54	$TlAsS_2$ (*Lorandite*)	1.8 (689)	1.52	-0.28	2
WO_3 (*Tungstinite, Meymacite, Hydrotungstite*)	2.7 (459)	3.5	0.8	0.43	WS_2 (*Tungstenite*)	1.35 (918)	1.77	0.42	2
Yb_2O_3	4.9 (253)	3.48	-1.42	8.15	ZnS (*Sphalerite*)	3.6 (345)	2.62	-0.98	1.7
$YFeO_3$	2.6 (476)	2.46	-0.14	7.81	ZnS_2	2.7 (459)	2.47	-0.23	2
ZnO (*Zincite*)	3.2 (247)	2.95	-0.25	8.8	$Zn_3In_2S_6$	2.81 (441)	1.98	-0.85	2
$ZnTiO_3$	0	-0.17	-0.17	7.31	ZrS_2	1.82 (681)	1.67	-0.15	2
ZrO_2 (*Baddeleyite*)	5 (248)	3.97	-1.03	6.7	---	----	----	---	---

[a]-pH_{zpc} for which the net adsorbed charge within the Helmholtz double layer [98,99] is equal to zero.

The data gathered above (Table 1) can be discussed in a very simplified and condensed way: Minerals of $\mathbf{E_{BG}} \leq$ *ca.* 3.3 eV (380 nm) possess the visible-light-driven photocatalytic activity (VLD). The oxide minerals are strong photo-oxidation catalysts in aqueous solutions, but are limited in their reducing power. The majority of metal oxide semiconductors have valence band edges ($\mathbf{E_{VB}}$) in the range 1 to 3 V above the H_2O reduction potential (relative to the electrochemical, SHE scale [96,97]), energies for conduction band edges ($\mathbf{E_{CB}}$) are close to, or less negative than, the H_2O reduction potential. More specifically, the electron generated in CB can reduce the substance if $\mathbf{E_{CB}}$ is more negative than the reduction potential of the substance (reactant) ($\mathbf{E_r}$) (*i.e.* $\mathbf{E_{CB}} < \mathbf{E_r}$). Similarly, the h^{+}_{VB} generated in the valence band can oxidize a substance if its reduction potential is lower than $\mathbf{E_{VB}}$ of semiconductor (*i.e.* $\mathbf{E_{VB}} > \mathbf{E_r}$). One should note that none of the minerals (which are presented in Table 1), upon the light exposure can promote electrons to CB, generating e^{-}_{CB}, which is able to reduce H_2O and become the hydrated electron (e^{-}_{aq}) of reduction potential $E^{\ominus}_{aq/e^{-}_{aq}}$ equal to -2.87 V [100]. Such electron cannot escape into and migrate throughout the solution, thus its reactions are limited to the immediate vicinity of the surface (see discussion in [101]). It should be noted that if **E_{CB}** < 0 V, e^{-}_{CB} can reduce H_3O^+-cation to molecular hydrogen (H_2), since reduction potential of SHE ($E^{\ominus}_{\mathrm{H^+/H_2}}$) is by definition equal to 0 V [96,97]. On the other hand, in the majority of minerals in Table 1, the light-induced promotion of electron to CB creates h^{+}_{VB} with **E_{VB}** higher than $E^{\ominus}_{\mathrm{^{\bullet}OH/OH^-}}$ = 1.9 V [100], allowing oxidation of OH^--anion to $^{\bullet}OH$-radical. As one can see, for much smaller number of minerals, h^{+}_{VB} has the reduction potential higher than $E^{\ominus}_{\mathrm{^{\bullet}OH,H^+/H_2O}}$ = 2.73 V [100], allowing oxidation of H_2O in neutral or acidic solution. Please note that non-transition metal sulphides generally have both **E_{CB}** and **E_{VB}** of higher energies than metal oxides; therefore, h^{+}_{VB} here are less oxidizing, but e^{-}_{CB} are rarely reducing. While, most transition-metal sulphides are characterized by small **E_{BG}** (< 1 eV, *ca.* 1340 nm) with both the oxidizing power h^{+}_{VB} and the reducing power of e^{-}_{CB} lower than those of non-transition metal sulphides.

Additionally, one has to bear in mind that both **E_{CB}** and **E_{VB}** are pH-dependent, since the ion balance on the mineral's surface is affected by the pH. Thus the oxidising power of h^{+}_{VB} and the reducing power of e^{-}_{CB} will also depend on the pH. For semiconducting metal oxides, the **E_{CB}** and **E_{VB}** vary with pH, following the Nernstian relation 4 [26,81]

$$E_{\mathrm{CB(orVB)}} = E^{\ominus}_{\mathrm{CB(orVB)}} + 2.303\frac{RT}{F\times(\mathrm{pH}_{\mathrm{zpc}}\text{-}\mathrm{pH})} \qquad (4)$$

where $E^{\ominus}_{\mathrm{CB(orVB)}}$ are the potential at the pH of the zero point of charge (**$\mathrm{pH_{zpc}}$**) the net adsorbed charge within the Helmholtz double layer [98,99] is zero). Thus pH has to be taken into account, since its increase not only results in lower concentration of H^+, which is the major electron scavenger, but also shifts **E_{CB}** of minerals toward more negative values (Figure **1**).

4. Resistance of Persistent Organic Pollutants and Pathogenic Microorganisms to Oxidative- and Bio-Degradation. Potential Risk from by-Products of an Incomplete Process

Here, we should emphasize that research on decontamination of aqueous solutions containing persistent organic pollutants has been the core of photocatalytic research for years (see for example a review [102].) However, research and commercial application were focused mainly on chemical impurities of significant contribution in terms of elimination of pathogenic microorganisms (since antibiotics are becoming less effective due to antimicrobial resistance). Thus, in addition to the researches focused on antimicrobial nanomaterials to inhibit bacterial growth and destroy the cells, many photocatalytic disinfection studies have been performed involving bacteria, fungi, algae and viruses [63,64,103–117]. Numerous experimental and review papers have been published. Particularly worth recommending is the relatively recent review on application of photocatalysis for toxicity reduction of real wastewaters [118], and elimination of viruses [119].

With few exceptions, like per- and polyfluorinated substances (PFASs) [101,120], the ROSs generation in photocatalysis very effectively induces oxidative decomposition of pollutants, which can even lead to their complete mineralization [5,14]. Therefore, one can hypothesize that the photocatalysis processes on the soil surface will take part in natural oxidative-reduction processes occurring in soil [84], and as such may contribute to its decontamination. However, a complete mineralization (*i.e.* formation of CO_2, H_2O and NH_3, exclusively) of the pollutant seems essential in many cases, since degradation products have the potential to be as harmful, or even more harmful toxins than the parent compounds.

The persistent micro-pollutants are frequently eliminated from the waste applying multi-stage process where so-called advanced oxidation processes (AOPs) [6] are usually used prior to biological stage to initially decompose the pollutants [121,122]. The micro-pollutants leftovers can appear incidentally even in the municipal waste, where the AOPs pre-treatment may potentially worsen situation due to formation of novel toxins upon oxidation. For instance, this appears to be the case for phenylurea derived compounds like herbicides such as *Linuron*, *Diuron*, and *Metobromuron* or the antimicrobial additive of personal care products *Triclocarban* [123–131]. The phenylurea herbicides production and use on beans, soybeans, tomatoes, tobacco, potatoes, flax, and sunflowers, will result in its release to the environment through various waste streams. If released to soil, the phenylurea herbicides will have moderate mobility. Volatilization of them should not be important, thus the herbicides may be degraded on soil surfaces. Research shows that some wastewater bacteria are able to hydrolyze the urea bridge in phenylurea herbicides producing mono- and dichloroanilines [131–135]. The fate of these metabolites is not certain, however they may slowly decompose, as well as bioaccumulate or bind to soil particles and undergo auto-oxidation [136]. This is of special importance since chloroanilines have been named 'probable carcinogens' by the U.S. EPA due to their association with bladder cancer[27-29] [137–139]. The environmental toxicity of *Linuron* and its metabolites had been partially eliminated with its replacement by *Metobromuron*. However, our laboratory study and computational predictions for both herbicides (*Linuron* and *Metobromuron* as well*)* foresees formation of similar hazardous products upon the AOPs treatment [126,140–142]. Among them are cyanates *e.g.* isocyanatomethane (methyl isocyanate, MIC, CH_3-N=C=O) - the toxin accused of causing nearly 3800 deaths in the *Bhopal disaster* [177][35]. Therefore, the suspicion that trace amounts of MIC could be formed during incomplete degradation of linuron-like pesticides ought to raise legitimate concerns.

Even when the situation is not so dramatic, peculiar products of the AOPs-reactions can avoid subsequent biodegradation. Moreover, such contamination may be significantly harmful or even destroy successive, biological stages of waste decontamination [122,141,143].

It appears that disinfecting of wastewater is an easier process than the elimination of persistent organic pollutants. On the 'molecular level' the processes of disinfection / hygienization of waste lead to decomposition of the natural, organic compounds, which are essential for pathogen survival and multiplication.

That should cause to death and elimination of harmful pathogens [144]. Individual molecules of proteins, lipids, sugars, and nucleic acids are relatively unstable and quite easily oxidized and hydrolysed [145–151]. However, living cells are able to regenerate oxidative damage quite efficiently through enzymatic and non-enzymatic repair processes [152]. (Pathogens with increased resistance may also be selected as a result.) Therefore, one have to keep in mind that reduction of the pathogen population to a level corresponding to the requirements imposed by regulatory institutions (see [153]) will require an oxidation process of high-intensity. It is unlikely that will be achievable in natural conditions because only a small portion of solar light's energy can be utilized in photocatalytic processes, which is evident from the comparison of E_{BG} values, shown in Table 1, with well known spectrum of sunlight (see *http://www.astm.org/ASTM*).

5. Interference of Redox Processes by Soil Organic Matter. Impact of Humic Acids on the Effectiveness of Photocatalysis

Soil Organic Matter (SOM) is one of the key elements of carbon circulation in nature [154,155]. SOM seems to be the most valuable part of the soil from an agricultural perspective but also for growth of natural vegetation cover [83,156]. It consists mainly humified organic debris of plants and other organisms as well as labile organic compounds derived from exudates of soil microorganisms and plant's roots. Numerous functions are performed by SOM in soil: starting from physical functions (stabilization of soil structure, water retention, thermal properties) [156–160]; throughout chemical functions (retention of cations, buffering capacity and pH effects, chelation of metals, interactions with xenobiotics); ending with the biochemical functions such as reservoir of metabolic energy, source of macronutrients, ecosystem resilience [156,158], or even allelopathy [161]. Interestingly, the reducing environment of humic acids promotes the formation of metallic and oxide nanoparticles in both laboratory and natural conditions [78,162,163].

From the point of view of the environment decontamination an interesting feature is the immobilization of inorganic substances as a result of formation of complexes with inorganic cations. For example, humified organic matter and polyvalent metal cation complexes take part in the

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formation of micro-aggregates with clusters and silt particles, oxides, and aluminosilicates [157]. On the other hand the immobilization of toxic to plants noble metals, by humic acids of peat, in the form of metal nanoparticles was observed [162,164] and confirmed in laboratory condition [78,165–167]. Unfortunately water-soluble humic acid (HA) compounds in the disinfection processes of drinking water and wastewater are considered as precursors of highly toxic, carcinogenic and mutagenic disinfectant by-products [168,169]. The chemistry of processes leading to the formation of toxic derivatives of HA has been previously extensively studied, and described in the basic works on radical chemistry of aromatic compounds [170–172]. HA are poly-aromatic compounds that have a variety of components including quinone, phenol, catechol, and sugar moieties [173,174], with significant antioxidant properties and the ability to scavenge free radicals [174–193].

The strong inhibitory effect of natural organic matter is also a major challenge for photocatalytic water purification. This organic matter can scavenge photogenerated h^{+}_{VB}, e^{-}_{CB} and radicals, and occlude ROS generation sites upon adsorption. Additionally, quantum efficiency of photocatalysis can be reduced due to absorption of light by organic compounds, when the light-quantum has too low energy to cause dissociation of chemical bonds, and its absorption causes the solution to only heat up [194]. The fact that humic acids scavenge •OH radicals and its precursor h^{+}_{VB}, desired when photocatalysis is used for degradation of humic acids, causes a decrease in the effectiveness of photocatalysis when its purpose is to degrade other pollutants [181]. A large contribution has been made to improve the quality of drinking water, thanks to the development of organic matter removal methods [195–200]. In this trend, works dedicated to increasing of the photocatalysis' efficiency counteracting the inhibitory effect of humic acids by decreasing the HA surface-adsorption and mitigation of the e^{-}_{CB} - h^{+}_{VB} recombination, were also created [201–203].

6. The Perspectives Photocatalysis on Soils Minerals 'In Vivo'

Soil is a major component of the Earth's geosystem, constitutes the outer layer of the lithosphere (continental crust). Soil-forming factors include climate, relief, parent material (bedrock), organisms (plants, animals, fungi and human being) and ground water, they all interact over the time [204–207].

Soil consists not only a solid phase (minerals and organic matter), but also a porous phase (gases and water). Usually, the solid phase consists half part of the soil, thus significantly affecting physical and chemical properties.

The continental crust is characterized by a huge variability of minerals and rocks. Because they are a soil substratum, the elements derived from weathering form soil's chemical composition. The elements found in the continental crust are divided into three groups depending on the average occurrence (Clarke number [207]). The first group consists of element with high Clarke number, which constitute the main mass of rocks and soils. This group includes: O, Si, Al, Fe, Ca, Na, K, Mg, C, H, S, P and Cl [208]. They determine geochemical properties of the landscape, mainly the conditions for the migration of other elements [209]. The second group is low Clarke number elements. Their migration depends on the conditions created by the elements of the first group. The last group is rare elements, whose content in continental crust is lower than 0.01%.

Iron as a first group element commonly occurs in the soil. The Fe content in continental crust is between 4.1-5.1%, depends on whether its mass or weight share is calculated [206,210]. Iron oxides are considered to be chemical compounds with great potential in photocatalytic. Similarly, is with Ti (0.3-0.6%, second group) [211]. These two semiconductors are quite common in soils, especially containing Fe, so there is a possibility to use the topsoil in the process of photocatalysis [192,212,213].

In addition to a photocatalyst, which is stable under given pH value and temperature conditions, for oxidation to sunlight occurs, the following are also necessary: solar light, atmospheric oxygen, and humidity. Soil surface is exposure to sunlight of the *ca.* 280 to 4000 nm range [214,215], so it has the ability to initiate solar energy conversion into chemical energy, therefore to control environmental pollution and decontamination [216,217].

Experimental research on the soils' usage in the decontamination of pollutants has been carried out several times [94,192,218]. The obtained results are promising, but are there opportunities to use this phenomenon outside the laboratory? There is no clear answer to this question yet. Under natural conditions, soil, as a complex component affected by many soil-forming factors, is characterized by significant variation of physical and chemical properties and undergoes many transformations. There are a number of crucial issues that would need to be resolved for widespread photocatalytic soil usage *in vivo*.

The supply of solar energy and oxygen is limited to the topsoil. In most climate zones, radiation is largely absorbed by the vegetation. In woody and shrubby vegetation zones, only a small part of the radiation reaches the soil surface [219]. Different situation is Earth' part with sparse vegetation, these are primarily the desert, semi-desert and tundra zones. The supply of solar energy is much higher, because of low soil shading [220,221]. In the polar climate (tundra zone), the radiation is limited with large seasonal variability, including polar nights [222]. On deserts and semi-deserts, the supply of energy is significant and is not disturbed by clouds cover. This is a consequence of low humidity and high atmospheric pressure. In these areas the soil cover is thin or not present at all. On the surface there are different rocks and minerals (sands, clays etc.). In the Temperate Climate Zone, the soil surface is covered by vegetation almost all year long. Only agricultural areas before the plant growing season (usually from October till April) are not covered by vegetation. Other issue in the variability of soil surface. Mostly relief is not flat, so there is a variation in the supply of energy to the surface. In the Northern Hemisphere, the northern slopes are less exposed to the sunlight than the southern slopes. That affects the soil properties, such as thickness, moisture and nutrients' content [223]. The solar radiation depends on the height of the sun above the horizon, which varies depending on the season. For example, the sun angle for Warsaw (42°N, Poland) difference between December and June is more than 45 degrees. (To get an overall, global picture of solar energy supplied to the Earth's surface, the reader can go to the handbook [214], and to the online interactive maps on the '*World Bank.* ***Global Solar Atlas'*** web page [222].)

The presence of Fe oxides in the soils is a fact, but their content varies both spatially on a global scale, as in the soil profile [224–226]. Fe evolution in soils is controlled both by natural factors (rock weathering, pedogenic processes driven), causing Fe transformation and translocation within and from soil (eluviation-illuviation, reduction-oxidation processes) [227], and human impact (industry, agriculture) [228].

Assuming that the photocatalysis occurs only in the surface, the presence of free oxides in the topsoil (humus horizon) is negligible. Their greatest accumulation occurs in horizons, such as *ferralic*, *nitic* or *cambic* which occur deeper in soil profile [229]. Hence, soils in which Fe oxides are abundant are mainly tropical and subtropical soils, such as Ferralsols and Nitisols. In the humus horizon, the content of Fe oxides is lower, due to accumulation by humus, which constitutes the sorption complex of the soil.

The diversity of soils on the Earth means that the environmental conditions, such as climate, parent material, relief, vegetation should be included in experiments of photocatalytic properties and deeply studied in the future. The potential of the soils is huge, they can be used as the basis of more sustainable alternative, instead of synthetic materials for decontamination of the pollutants.

7. Summary and Conclusions

The upper layers of the lithosphere can be a good source of unique semi-conducting materials of natural photocatalytic properties. A combination of many factors is required for the photocatalysis process to be effective. Particular requirements such as adequate, intensive and long-lasting sunlight, the presence of specific minerals, moderate humidity of the soil solution (see above) make, that under natural conditions photocatalytic processes cannot be fully effective. It cannot be ruled out that decontamination of desert soils can, in part, be attributed to photocatalysis, which can result in mineralization of organic matter. One can put forward the thesis that the probability that in this way Nature without the support of technology will cope, for example, with the pesticide residues or pathogenic microorganisms is very small. In practice, these processes call for highly advanced technical solutions. In rare circumstances, effective photocatalysis can occur spontaneously without human intervention. A forward-looking idea seems to be usage of natural photoactive minerals in new and existing technologies utilizing the photocatalytic process. The applications that are cited in the [119] work, such as building materials cement-based products, ceramic tiles, bituminous membranes etc. can be good examples.

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used “Conceptualization, D.P. and A.S.; writing—original draft preparation, D.P., A.S. J.K., K.H., M.C.; writing—review and editing, D.P.; supervision, D.P.; All authors have read and agreed to the published version of the manuscript.” Please turn to the CRediT taxonomy for the term explanation. Authorship must be limited to those who have contributed substantially to the work reported.

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List of Abbreviations

Allelopathy	chemically-mediated competition between plants
AOPs	Advanced Oxidation Processes
AVS	Absolute Vacuum Scale
C B	Conduction Band
E_{BG}	Band-gap Energy
E_{CB}	Energy of Conduction Band
$E^{\ominus}_{Ox/Red}$	Standard Reduction Potential of the Ox/Red pair
E_r	Reduction Potential of Reactant
E_{VB}	Energy of Valence Band
MIC	isocyanatomethane (methyl isocyanate, CH_3-N=C=O, CAS No. 624-83-9)
NOM	Natural Organic Matter
PFOSs	Perfluorinated Organic Surfactants
pH_{zpc}	the net adsorbed charge within the Helmholtz double layer
POPs	Persistent Organic Pollutants
SHE	Standard Hydrogen Electrode
SRP	Standard Reduction Potential
VB	Valence Band

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