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Review

THE USE OF LOW COST ADSORBENTS FOR PURIFICATION WASTEWATER

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Adsorption is one of the effective methods of advanced wastewater treatment, which industries employ to reduce hazardous organic and inorganic wastes in effluents. The use of low cost adsorbent has been investigated as a replacement for current costly methods of removing toxic substances from wastewater. In this article, the use of low cost adsorbents for the removal of toxic substances from wastewater has been reviewed.
Key words: adsorption, heavy metals, low cost adsorbents, waste water.

Upotreba jeftinih adsorbensa za pročišćavanje otpadnih voda. Adsorpcija je jedna od djelotvornih metoda za napredno pročišćavanja otpadnih voda industrije kojom se smanjuju opasni organski i anorganski otpadni ispusti. Istražuje se upotreba jeftinih adsorbensa u zamjenu za trenutno skupljim metodama uklanjanja toksičnih tvari iz otpadnih voda. U ovom radu prikazan je pregled upotrebe jeftinih adsorbensa za uklanjane toksičnih tvari iz otpadnih voda
Ključne riječi: adsorpcija, teški metali, jeftini adsorbensi, otpadna voda.

INTRODUCTION

The current pattern of industrial activity alters the natural flow of materials and introduced novel chemical into the environment. The rate at which effluents are discharged into the environment, especially water bodies, have been on the increase as a result of urbanization. Most of these effluents contain toxic substances especially heavy metals, dyes, phenols etc [1]. The heavy metals containing industrial wastewater can cause serious environmental pollution problems for aquatic life. The main industrial sources of toxic metal contamination in wastewater include: electroplating, metal finishing, metallurgical, tannery, chemical manufacturing, mining and battery manufacturing industries. Some heavy metal are necessary in small amounts for normal development of biological cycles, however most of these heavy metals are becoming toxic at high concentration [2 - 10]. The presence of dyes in effluents is a major concern due to their adverse effect to many forms of life. The discharge of dyes in the environment is a matter of concern for both toxicological and esthetical reasons. Industries such as textile, lather, paper, plastic, use dyes in order to colour their

products and also consume substantial volumes of water [3 -12]. Phenolic compounds are considered to be hazardous wastes, which are released into the aquatic environment by industries such as coke ovens in steel plants, petroleum refineries, petrochemical, phenolic resin, and fertilizer pharmaceutical, chemical and dye industrial and have been reported in hazardous wastes sites [13].

A large number of methods (conventional ion exchange, adsorption, electrolytic or liquid extraction, electrodialysis, chemical precipitation, membrane filtration) have been developed for decontamination of industrial waters [14 - 24]. Adsorption is a well known equilibrium separation process and an effective method for water decontamination applications [25 - 29]. Adsorption has been found to be superior to other techniques for purification water in flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [3]. Cost is an important parameter for comparing the adsorption materials. However, cost information is seldom reported, and the expense of individual adsorbents varies depending on the degree of processing required and local availability. In general, an adsorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by product or waste material from another industry.

This review provides a summary of available information on a wide range of potentially low cost adsorbents.

Activated carbon

Though commercially available, activated carbon is usually derived from natural materials such as biomass, lignite or coal, but almost any carbonaceous materials may be used as precursor for the preparation of carbon adsorbents [30 - 35]. Based on its size and shape, activated carbon is classified into four types: powder, granular, fibrous and clothe. Activated carbon has been popular choice as an adsorbent (the best adsorbent) for the removal of toxic substances from wastewater but its high cost poses an economical problem. Figure 1 shows schematic presentations and the SEM image of the structure activated carbon.

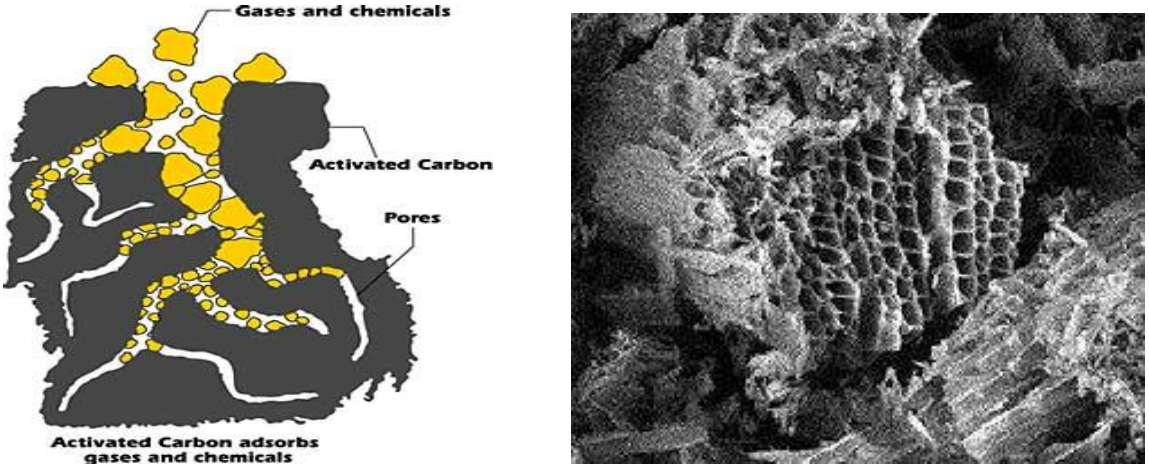

Figure 1. Schematic presentations and the SEM image of the structure activated carbon
Slika 1. Shematski prikaz i SEM slike strukture aktivnog ugljika

Review of low cost adsorbents

Lignin

Lignin is a natural amorphous cross – linked resin that has an aromatic three – dimensional polymer structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, and aldehyde groups, making it potentially useful as an adsorbent material for removal of heavy metals from water [36]. Suhas et al. [37] have reviewed the literature on lignin as a biosorbent. Sarivasta et al. [38] obtained remarkably high uptake of Pb (II) and Zn (II), up to 1587 and 73 (mg / g) for Pb (II) and Zn (II), respectively, by using lignin extracted from black liquor.

Clays

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fractions of soils, sediments, rocks and water and may be composed of mixture of fine grained clay mineral sand clay – sized crystals of the minerals such as quartz, carbonate and mineral oxides. The adsorption capabilities of clay results from a net negative charge on the structure on fine – grain silicate minerals. This negative charge in neutralized by the adsorption of positively charges species, giving clay the ability to attract and hold cations such as heavy metal. The large surface area of clays (up to 800 m^2 / g) also contributes to the high adsorption capacity [39]. Some of the reported capacities for clay are show in Table 1.

Table 1. Reported adsorption capacities for clay
Tablica 1. Prikaz adsorpcijskog kapaciteta gline

Adsorbat	Cr (VI)	Pb (II)	Cd (II)	Methylene blue
Capacity (mg / g)	55	58	16.5	300

Zeolites

Basically zeolites are a naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules, linked with each other by shared oxygen atoms. Zeolite consists of a wide variety of species such as clinoptilolite and chabazite. In 1990, the removal of heavy metals from wastewater using clinoptilolite was studied. The selectivity of the series of the heavy metals studied was determined to be as follows [44]:

Pb (II) > Cd (II) > Cu (II) > Co (II) > Cr (III) > Zn (II) > Ni (II) > Hg (II)

The adsorption properties of zeolites are the results of their ion-exchange capabilities. The three-dimensional structure of zeolite possesses large channels containing negatively charged sites resulting from heavy metal ions replacement of Si (IV) in the tetrahedral (Figure 2). Sodium, calcium, potassium and other positively charged exchangeable ions occupy the channels within the structure and can be replaced with heavy metals [45].

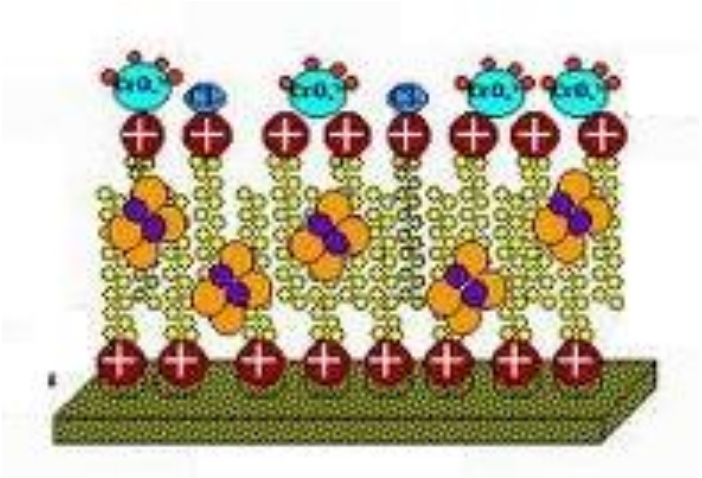

Figure 2. Schematic presentations of zeolite activated sites
Slika 2. Shematski prikaz aktivnih mjesta na zeolitu

Bark, sawdust an other tannin – rich materials

Bark is available as a by – product of the timber industry. Bark is effective because of its high tannin content. The polyhydroxy polyphenol groups of tannin are thought to be the active species in the adsorption process. Ion exchange takes place as metal cations displace adjacent phenolic hydroxyl groups, forming a chelate [46]. Another waste product from the timber industry is sawdust. Bryan et al. [47] showed adsorption of copper u and hexavalent chromium by red fir sawdust taking place primarily on components such as lignin or tannin rather than onto the cellulose backbone of the sawdust. Adsorption capacity is very high. It was suggested that sawdust is a good adsorbent for the removal of copper and chromium [48].

Carbon anode dust

In the Hall-Heroult process aluminium is produced by the electrolytic reduction of alumina dissolved in an electrolyte containing cryolite. For reduction, carbon anode has been used. The remaining parts of spent anodes from the aluminium production are called anode butts. There are two anode butts, the raw anode butts and the pre-baked anode butts. The cleaned anode butts are crushed and reused in the production of new anodes (about 20 % of the anode is recycled). The carbon anode dust originates from the baking and transport process of anodes and is not recycled [49, 50]. This is non-toxic waste material that has to be disposed on the specially arranged depots.

Waste mould sand

In foundry industry, millions tones of spent materials are disposed in the world [51]. Over 70 % of the amount of the dumped waste materials consists of sands. For many years, the spent sands generated by foundry industry were successfully used as landfill materials. But disposal by landfill of spent sands is becoming an increasing problem as legislation is getting tighter. Also the disposal costs by current practices increases rapidly [52]. This waste mould sand is composed of fine silica sand, clay

binder, organic carbon, and residual iron particles. Because of their potential adsorptive properties, waste mould sand can use as a low cost adsorbent [53].

Blast furnace slag, electric furnaces slag and blast furnace sludge

Blast furnace slag is industrial by – product in the production of pig iron which causes a disposal problem. Recently, it was converted into an effective adsorbent and used for the removal of a dye and metal ions. Electric furnace slag is nearly any solid which melts and forms a silicate glass during a metal refining process [54].

Blast furnace sludge is a by – product of the steel – making industries. Indoor recycling poses problems due to small particle size (<0.1 mm) and to the presence of lead, zinc and alkaline metals. The dried blast furnace sludge consists of iron oxides and coke as the major phases. Its high iron oxide and coke content may enable its use as a metal adsorbent in industrial wastewater purification processes [55]. The resulting adsorption capacities for these adsorbents are presented in Table 2.

Table 2. Reported adsorption capacities (mg / g) for metallurgical adsorbents
Tablica 2. Prikaz adsorpcijskog kapaciteta (mg /g) za metalurške adsorbense

Adsorbents	Cr (VI)	Ni (II)	Pb (II)	Zn (II)	Cd (II)
Carbon anode dust	4.29	8.64			
Waste mould sand	1.19	2.53			
Blast furnace slag			7.50	4.26	6.74
Electric furnaces slag			33.78		

Other adsorbents

Waste iron (III) hydroxide is one of waste from fertilizer industries. It has been extensively investigated for removing Cr (VI) from wastewater [58]. It was reported that the maximum adsorption capacity of iron (III) hydroxide was found to be 0.47 mg / g.

Waste slurry is also one the industrial by – product generated in fertilizer plant showing god adsorptive capacities [58].

Red mud, a by – product of the aluminium industry, is composed mainly of the particles of silica, aluminum, iron, and titanium oxide. It was found that an adsorption capacity of 1.6 of Cr (VI) / g red mud was achieved at pH of 5.2 [59].

Dead biomass accumulates heavy metals to an equal or greater extent than living cell. The bacterial cell surfaces are anionic due to the presence of ionized groups in the cell wall polymers, causing the cell to attract metal cations. Removal of dye by biomass has been the subject of many recent researches. It has been found that bioadsorbents derived from suitable algal biomass can be used for the effective removal of methylene blue from aqueous solutions [3]. Diatomite is a siliceous sedimentary rock consisting principally of the fossilized skeletal remains of the diatomite, a unicellular photosynthetic plant

related to algae. It is no pure hydrous silica but rather contains other associated elements; alkaline earth and alkali metals. The diatomite surface contains silanol groups that spread over the matrix, which is a very active group and it can react with many polar inorganic and organic compounds and various functional groups. In recent years, natural diatomite surface may be modified with both inorganic and organic reagents have been used in other areas, notably in clean technology e. g. separation of trace heavy metals from aqueous or non-aqueous systems. Large quantities of waste microbial biomass are produced in many industries such as citric biosynthesis and penicillin production [60 – 62].

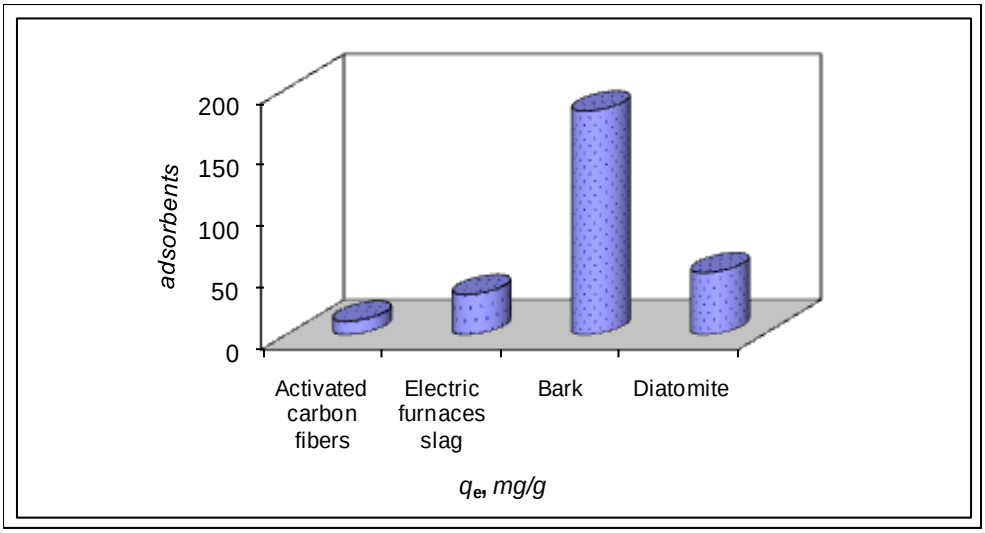

Figure 3. The dependence of adsorbents capacity on the type of adsorbents (adsorbat Cu (II) ions)
Slika 3. Ovisnost kapaciteta adsorpcije o vrsti adsorbensa (adsorbat Cu (II) ioni)

CONCLUSIONS

We have reviewed the sources and toxic substance as well as the reason why they need to be removed from our environment. Conventional methods of removal are expensive; hence the use of low cost abundant environmentally friendly adsorbents were reviewed. Low cost, effective, readily available materials can be used in place of activated carbon or ion exchange resins for the removal of toxic substances from solutions.

In addition, if the alternative adsorbents mentioned previously are found highly efficient for heavy metal removal, not only for industries, but the living organisms and the surrounding environment will also benefit from the decrease or elimination of potential toxicity of the heavy metal. Thus, the use of low-cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future.

REFERENCES

[1] J. C. Igwe, A. A. Abia, Africal J. Biotech., 5 (2006), 1167-1179.

[2] O. Gulnaz, S. Saygideger, E. Kusvuran, J. Hazard. Mater. B120 (2005), 193-200.

[3] S. H. Lin, R. S. Juang, J. Hazard. Mater. B92 (2002), 315-326.

[4] L. H. Wartelle, W. E. Marshall, Adv. Environm. Res. 4 (2000), 1-7.

[5] N. Bektas, S. Kara, Sep. Purif. Technol. 39 (2004), 189-200.

[6] I. Kula, M. Ugurlu, H. Karaoglu, A. Celik, Bioresour. Technol. 99 (2008), 492-501.

[7] C. C. V. Cruz, A. C. A. Costa, C. A. Henriques, A. S. Luna, Bioresour. Technol. 91 (2004), 249-257.

[8] O. Gulnaz, S. Saygideder, E. Kusvuran, J. Hazard. Mater. B120 (2005), 193-200.

[9] D. Aggarwal, M. Goyal, R. C. Bansal, Carbon 37 (1999), 1989-1997.

[10] N. Ortiz, M. A. F. Pires, J. C. Bressiani, Waste Manag. 21 (2001), 631-635.

[11] M. Rafatullah, O. Sulaiman, R. Hashim, A. Ahmad, J. Hazard. Mater. 177 (2010), 70–80.

[12] I. A. Tan, A. L. Ahmad, B. H. Hameed, J. Hazard. Mater. 154 (2008), 337-346.

[13] M. Ahnaruzzaman, D. K. Sharma, J. of Colloid Interface. Sci. 287 (2005), 14-24.

[14] H. A. Qdais, H, Moussa, Desalination 163 (2) (2004) 105-110.

[15] A. K. Chakravarti, S. B. Chowdhury, S. Chakrabarty, T. Chakrabarty, D. C. Mukherjee, Colloid. Surface A. 103 (1995), 59-71.

[16] F. Gode, E. Pehlivan, Fuel Process. Technol. 86 (2005) 875-884.

[17] K. S. Low, C. K. Lee, A. Y. Ng, Bioresour. Technol. 68 (1999), 205-208.

[18] S. Lacour, J. C. Bollinger, B. Serpaud, P. Chantron, R. Arcos, Anal. Chem. Acta 428 (2001) 121-132.

[19] H. Leinonen, J. Lehto, React. Functional Polym. 43 (2000), 1-6.

[20] M. Dakiky, M. Khamis, A. Manassra, M. Mereb, Adv. Enviroment. Researc. 6 (2002), 533-540.

[21] S. Karabulut, A. Karabakan, A. Denizli, Y. Yurum, Sep. Purif. Technol. 18 (2002), 177-184.

[22] L. J. Yu, S. S. Shukla, K. L. Dorris, A. Shukla, J. L. Margrave, J. Hazard. Mater. B 100 (2003), 53-63.

[23] J. Q. Jiang, C. Cooper, S. Ouki, Chemosphere 47 (2002), 711-716.

[24] M. A. Ferro – Garcia, J. Rivera – Utrilla, J. Rodriguez – Gordillo, I. Bautista – Toledo, Carbon 26 (1988), 363-373.

[25] A. Dabrowski, Adv. Colloid Interface Sci., 93 (2001), 135-224.

[26] A. Ahmad, M. Rafatullah, M. Danish, Holz als Roh – und Werkstoff, 65 (207), 429-436.

[27] A. Ahmad, M. Rafatullah, O. Sulaiman, M. H. Ibrahim, Y. Y. Chii, B. M. Siddique, Desalination 247 (2009), 636-646.

[28] M. Rafatullah, O. Sulaiman, A. Ahmad, J. Hazard. Mater. 170 (2009), 969-977.

[29] E. N. El. Qada, S. J. Allen, G. M. Walker, Chem. Eng. J. 135 (2008), 174-184.

[30] G. G. Stavropoulos, A. A. Zubaniotou, Microporous Mesoporous Mater. 82 (2005), 79-85.

[31] B. Bestani, N. Benderdouche, B. Benstaali, M. Belhakem, A. Addou, Bioresour. Technol. 99 (2008), 8441-8444.
[32] M. J. Iqbal, M. N. Ashiq, J. Hazard. Mater. B139 (2007), 57-66.
[33] N. Kannan, M. M. Sundarm, Dyes Pigments 51 (2001), 25-40.
[34] K. V. Kumar, S. Sivanesan, J. Hazard. Mater. 134(2006), 237-244.
[35] A. N. Fernandes, C. A. P. Almeida, C. T. B. Menezes, N. A. Debacher, M. M. D. Sierra, J. Hazard. Mater. 144 (2007), 412-419.
[36] X. Guo, S. Zhang, X. Shan, J. Hazard. Mater. (2007), doi: 10.1016/j.jhazmat.2007.05.065.
[37] P. J. M. Carrott, M. M. L. Ribeiro Carrott, Bioresour. Technol. 98 (2007), 2301-2312.
[38] S. K. Srivastava, A. K. Singh, A. Sharma, Environ. Technol. 15 (1994), 353-360.
[39] F. Cadena, R. Rizvi, R. W. Peters, (1990) Feasibility studies for the removal of heavy metals from solution using tailored bentonite. In Hazardous and industrial Wastes, Proceedings of the Twenty – Second Mid-Atlantic Industrial Waste Conference, Drexel University, pp. 77-94.
[40] T. C. Yang, R. R. Zall, Ind. Eng. Chem. Prod. Res. Dev. 23 (1984), 168-172.
[41] S. A. Khan, A. Riaz – ur- Rehman, M. A. Khan, Waste Manage. 15 (4) (1995), 271-282.
[42] K. K. Panday, G. Prasad, V. N. Singh, J. Chem. Tech. Biotechnol. A 34 (1984), 367-374.
[43] M. Bagane, S. Guiza, Ann. Chim. 25 (2000), 615-626.
[44] M. J. Zamzow, B. R. Eichbaum, Sep. Sci. Tech. 25 (1990), 1555-1569.
[45] I. Santiago, V. P. Worland, E. Cazares-Rivera, F. Cadena (1992) Adsorption of heksavalent chromium onto tailored zeolites. 47th Purdue Industrial Waste Conference Proceedings, Lewis Publishers Inc., Chelsea, MI., pp. 669-710.
[46] J. M. Randal, E. Hautala, G. McDonald, J. Appl. Polymer Sci., 22(2) (1978), 379-387.
[47] P. S. Bryant, J. N. Petersen, J. M. Lee, T. M. Brouns, Appl. Biochem. Biotechnol. 34-35 (1992), 777-788.
[48] M. Ajmal, A. H. Khan, S. Ahmad, A. Ahmad, Water Res. 32 (1998), 3085-3091.
[49] K. Grjotheim, H. Kvande: Introduction to Aluminium Electrolysis, Understanding the Hall-Heroult Process, Aluminium-Verlag, Düsseldorf, (1993).
[50] J. Thonstad, P. Fellner, G. M. Haarberg, J. Hiveš, H. Kvande, A. Sterten: Aluminium Electrolysis Fundamentals of the Hall-Heroult Process, Aluminium-Verlag Marketing&Kommunikation GmbH, Düsseldorf, (2001).
[51] R. S. Dungan, N. H. Dees, J. Environ.Manage. 90 (2007), 1-10.
[52] S. Jl, L. Wan, , Z. Fan, Water, Air, and Soil Pollut. 132 (2001), 347-364.
[53] T. Lee, J. Park, J. Lee, Chemosphere 56 (2004), 571-581.
[54] L. Ćurković, Š. Cerjan-Stefanović, A. Rastovčan – Mioč, Wat. Res. 35 (2001), 3436-3440.
[55] S. E. Bailey, T. J. Olin, R. M. Bricka, D. D. Adrian, Wat. Res. 33 (1999), 2469-2479.
[56] A. Rađenović, J. Malina, A. Štrkalj, Ljevarstvo, 41(2009), 41-46.
[57] A. Štrkalj, A. Rađenović, J. Malina, RMZ – Materials and geoenvironment, 57(2010) (2), 165-172.
[58] C. Namasivayam, K. Ranganathan, Environ. Pollut. 82 (1992), 255-261.

[59] A. I. Zouboulis, K. A. Kydros, J. Chem. Technol. Biotechnol. 53 (1993,) 95-101.
[60] A. Chergui, M. Z. Bakhti, A. Chahboub, S. Haddoum, A. Selatnia, G. A. Junter, Desalination, 206 (2007), 179-184.
[61] S. Erenturk, E. Malkoc, Appl. Surf. Sci. 253 (2007), 4727-4733.
[62] S. R. Bai, T. E. Abraham, Bioresour. Technol. 79 (2001), 73-81.