



– A REVIEW

METAL/MIXED METAL OXIDES AND THEIR APPLICATIONS AS ADSORBENTS

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ABSTRACT

Metal oxides/mixed metal oxides have wide applications as catalyst, adsorbents, superconductors, semiconductors, ceramics, antifungal agents and also have spacious applications in medicines. This review article is focused on their applications as adsorbents in various organic reactions.

Key words: Metal, Metal oxide, Adsorbent.

INTRODUCTION

Metal oxides

Metal oxides play a very important role in many areas of chemistry, physical and materials science¹⁻⁸. Metal oxides are formed as a consequence of co-ordination tendency of metal ions so that oxide ions form co-ordination sphere around metal ions and give rise to close packed structure. The different physical, magnetic, optical and chemical properties of metal oxides are of great interest to chemists because these are extremely sensitive to change in composition and structure. Different metal/mixed metal oxides have been synthesized and further studied for their applications in diverse field⁹⁻²¹. Extensive studies of this relationship leads to a better understanding of the chemical bond in crystal. The metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior. The transition metals and their compounds are used as catalysts in chemical industry and in battery industries. Besides, these compounds can be used in formation of interstitial compounds and alloy formation. The transition metals have the

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special properties of formation of coloured compounds and show magnetic properties. Metals of d-block elements are used for many industrial applications. They behave as catalysts, superconducting materials, sensors, ceramics, phosphors, crystalline lasers etc. Besides these, they are excellent photoactive materials and work as photosensitizer. Mixed metal oxide (MMO) electrodes are devices with useful properties for chemical electrolysis. Metal/mixed metal oxides have wide applications as catalyst because of their high surface area and reactive sites. Number of scientists and academicians are using metal/mixed metal oxides as catalyst in various organic reactions.

Adsorbents

Metal/mixed metal oxides have wide application as adsorbents. Some of them are described here. Quan et al.²² synthesized removal of copper from aqueous solution using iron-containing adsorbents derived from methane fermentation sludge. Iron-containing adsorbents prepared from methane fermentation sludge (MFS) were characterized by N₂ adsorption, XRD, SEM, EDX, pH determination and elemental analysis. The desorption studies were also performed and the mechanisms of Cu(II) adsorption was proposed. The results indicated that the adsorbent obtained at 700°C for 1 h in a steam atmosphere possessed the highest capability for Cu (II) adsorption. The invisibility of copper adsorption on the iron containing adsorbents is attributed to the formation of strong bonds between Cu (II) and the iron (hydro) oxides. The adsorbent can be applied to remove copper from water or soil by fixation onto the surface. Wang et al.²³ used removal of impurities from copper electrolyte with adsorbent containing antimony. A new adsorbent was synthesized possessing not only the properties of common adsorbents, but also special merits of its own. The paper presents the results of adsorbent synthesis, characterization, regeneration, and metal ion separation. The feasibility of utilizing this adsorbent for copper electrolyte purification has been examined. Garces et al.²⁴ followed a new method for study of the adsorption function of an adsorbent applied to the study of the adsorption function of isopropyl alcohol on a zinc oxide catalyst. The sorbent's sorption capacity at breakthrough increased with the sulfidation temperature reaching 87% of the theoretical value for desulphurization at 400°C. A deactivation model that considers the activity of the solid reactant was used to fit the experimental data. Good agreement between the experimental breakthrough curves and the model predictions was obtained. Kolboe²⁵ prepared characterization and studied properties of iron oxide coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. Thermodesorption curves of isopropyl alcohol from a zinc oxide catalyst have been analyzed under the assumption that the Langmuir isotherm for a heterogeneous surface is a valid model. From visual inspection of the desorption curves, five sets of adsorption sites were assumed. Asare and Fuerstenav²⁶ discovered adsorption phenomena in hydrometallurgy, the uptake of copper nickel and

cobalt by oxide adsorbents in aqueous ammoniacal solutions. The uptake or adsorption of copper, nickel and cobalt by finely divided oxide solids in aqueous ammoniacal medium has been investigated experimentally in order to determine how adsorption on leach residues can affect the recovery of leachable metals. Adsorption behavior was found to have maxima and minima as a function of pH, the magnitude of which depends on ammonia concentration, the metal cation, and the adsorbent. Asare and Fuerstenav²⁷ developed adsorption phenomena in hydrometallurgy 3 model for copper, nickel and cobalt uptake. The uptake of hydrolysable ions by oxide adsorbents in aqueous ammoniacal solutions has been interpreted in terms of a mechanism involving the competitive adsorption of all the aqueous species. An adsorption model is presented which combines double layer theory with properties of the substrate (pzc, dielectric constant), the solvent medium (dielectric constant) and the aqueous ionic species (stability constants). Ning et al.²⁸ investigated the effect of zinc and cerium addition on property of copper based adsorbents for phosphine adsorption. A series of copper based activated carbon (AC) adsorbents were prepared in order to investigate the effect of Zn, Ce addition on Cu-based AC adsorbents for phosphine (PH₃) adsorption removal from yellow phosphorous tail gas. N₂ adsorption isotherm and X-ray diffraction (XRD) results suggested that the addition of Zn could increase the adsorbent ultramicropores, decrease the adsorbent supermicropores and the adsorbent average pore diameter. Therefore, it enhanced the PH₃ adsorption capacity. Appropriate amount of Ce addition could promote the reducibility of copper oxide, increase the thermal stability of adsorbent, and therefore enhance the PH₃ adsorption capacity. The present study indicated that the Cu-based adsorbents might be one of candidates for PH₃ removal from yellow phosphorous tail gas. Bose et al.²⁹ found that critical evaluation of treatment strategies involving adsorption and chelation for wastewater containing copper, zinc and cyanide industrial wastewater containing heavy metals and cyanide requires treatment for removal of both metals and cyanide before disposal. Conventional methods for treatment of such wastewater involve alkaline-chlorination for cyanide destruction, followed for pH adjustment for metal precipitation, and subsequent removal of precipitate by solid-liquid separation processes. The objective of the study described in this paper is to critically evaluate treatment strategies involving some indigenous adsorbents and a low-cost chelating agent for treatment of a simulated wastewater. The evaluation procedure involved comparison of the performance of these treatment strategies with that of conventional treatment. Pan et al.³⁰ reported reusing sewage sludge ash as adsorbent for copper removal from wastewater. The sewage sludge ash (SSA) can potentially be used for removal of heavy metals from wastewater due to its similar chemical composition to that of fly ash and blast-furnace silage. The adsorption test of applying SSA into synthetic wastewater revealed that the adsorption isotherm of SSA for copper ions generally followed the Langmuir model. The primary mechanisms of copper removal by SSA included electrostatic attraction, surface complex formation, and cation

exchange. Arias et al.³¹ examined competitive adsorption and adsorption of copper and zinc in acid soils. As an aid in evaluating the environmental threat posed by Cu and Zn when both are present in acid soils, competitive and noncompetitive adsorption of Cu and Zn onto samples of the surface horizon of eight such soils was measured in batch experiments carried out at pH 5 with 0.01 M NaNO₃ as background electrolyte. The Langmuir–Freundlich equation was not appropriate for these data. It could not be fitted to the Zn data, and when fitted to the Cu data, the uncertainty in the values of its parameters was too large for them to be useful. Desorption of Cu into NaNO₃ solution from previously Cu-loaded soils in no case exceeded 11% of the Cu previously adsorbed, whereas analogous desorption of Zn was in all cases greater and ranged from 9% to 32%. Tubrbeville and Yap³² reviewed the chemistry of copper containing sulphur adsorbents in the presences of mere tans. A brief review of the chemistry of copper and thiols is given and a contrast is made to the behavior of copper-containing adsorbents used for the desulfurization of liquid hydrocarbon streams that are routinely treated in refinery processes. At a temperature of approximately 150⁰C, very well formed lamellar crystals of copper (I) thiolate are formed, which indicates that the copper migrates from the surface of the catalyst to expose bulk copper for further reaction. Turan et al.³³ worked on adsorption of copper and zinc ions determination of the optimal conditions by the statistical design of experiments. In their study, a full factorial experimental design was utilized to access the effect of three factors on the adsorption of copper (II) and zinc (II) ions from an aqueous leachate of an industrial waste with little as adsorbent. In the adsorption kinetics models, the second order model best described the data. Illite was a reasonably effective adsorbent for Cu²⁺ and Zn²⁺ from aqueous leachates of industrial waste. Li et al.³⁴ reported preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. The preparation of chemically modified orange peel cellulose adsorbents and its biosorption behaviors of Co(II), Ni(II), Zn(II) and Cd(II) have been studied. Effects of different chemical modifications on the adsorbent properties were also observed including different alkalis saponification. The maximum adsorption capacities of Ni(II), Co(II), Zn(II) and Cd(II) for SPA, SPA, SCA and SOA were obtained as 1.28, 1.23, 1.21 and 1.13 mol/kg and have increased by 95, 178, 60 and 130%. The Langmuir and Freundlich adsorption isotherms models fitted the experimental data best with regression coefficient $R^2 > 0.95$ for all the metal ions. Elution efficiencies with different concentrations of HCl were evaluated. Polychronopoulou et al.³⁵ utilized novel Fe–Mn–Zn–Ti–O mixed metal oxides for the low temperature removal of H₂S from gas streams in the presence of H₂, CO₂ and H₂O. The efficiency of Fe–Mn–Zn–Ti–O mixed-metal oxides of varying composition prepared by sol–gel methods toward removal of H₂S from a gas mixture containing 0.06 vol% H₂S, 25 vol% H₂, 7.5 vol% CO₂, and 1–3 vol% H₂O was studied in the 25–100⁰C range. In particular, a three times greater H₂S uptake at 25⁰C compared with that on the commercial adsorbent was found. The work provides new fundamental knowledge

that could trigger further research efforts toward the development of alternative mixed metal oxide not based on toxic. Han et al.³⁶ evaluated characterization and properties of iron oxide coated zeolite as adsorbent for removal of copper (II) from solution in fixed bed column. A new composite adsorbent, iron, oxide coated zeolite (IOCZ), was characterized and employed for the removal of Cu (II) from aqueous solution using fixed bed column. The Thomas model was found suitable for the description of break through curve at all experimental conditions, while Adams-Bohart model was only for an initial part of dynamic behavior of the IOCZ column. The theoretical breakthrough curve was compared with experimental breakthrough curve profile in the dynamic process. Chen et al.³⁷ checked preparation and characterization of porous granular ceramic containing dispersed aluminium and iron oxide as adsorbents for fluoride removal from aqueous solution. Porous granular ceramic adsorbents containing dispersed aluminum and iron oxides were synthesized by impregnating with salt solutions followed by precipitation at 6000°C. Characterization studies on the adsorbent by SEM, XRD, EDS, and BET analysis were carried out to clarify the adsorption mechanism. The adsorbents were sphere in shape, 2-3 mm in particle size, highly porous and showed specific surface area of 50.69 sq m/g. The experimental data were well explained with pseudo-second-order kinetic model. Results from this study demonstrated potential utility of Al/Fe dispersed in porous granular ceramics that could be developed into a viable technology for fluoride removal from aqueous solution. Dellyanni et al.³⁸ analyzed modelling the sorption of metal ions from aqueous solution by iron based adsorbents. The possibility of using iron-based adsorbents (i.e. akaganeite or goethite) to remove heavy metal ions from aqueous solutions was the aim of the present review paper. Synthesized material was used in two forms, i.e. in fine powder of nanocrystals and in the form of grains (as granular). Typical adsorption models were discussed and the bed depth – service time equation has been applied to the sorption results in order to model the column operation. Wang et al.³⁹ discussed microwave-assisted preparation of bamboo charcoal based iron containing adsorbents for Cr (VI) removal. Bamboo charcoal-based, iron containing adsorbents (Fe-BC) was developed by using bamboo charcoal (BC) as a supporting medium for ferric iron that was impregnated by $\text{Fe}_2(\text{SO}_4)_3$ H_2SO_4 simultaneous treatment, followed by microwave heating. The results showed the BET specific surface area and total pore volume. The adsorption of Cr (VI) onto Fe-BC was spontaneous and exothermic under the studied conditions. Column adsorption experiment with Fe-BC showed that Cr (VI) could be removed to below 0.05 mg/L within 360 bed volumes at empty bed contact time 2 min when the groundwater containing approximately 0.12 mg/L of Cr (VI) was treated. Arora et al.⁴⁰⁻⁴² synthesized different metal oxides and observed their application in chemical evolution and origins of life through adsorption process. Tseng et al.⁴³ synthesized kinetics and equilibrium of adsorption removal of copper from magnetic polymer adsorbent. This study examined the desorption of copper ions, which were adsorbed on the magnetic polymer

adsorbent (MPA) of polyvinyl acetate-iminodiacetic acid (M-PVAC-IDA), by ethylenediamintertraacetic acid (EDTA). Stage-wide desorptions were applied to remove the Cu (II) ions from the Cu (II) adsorbed M-PVAC-IDA (A-M-PVAC-IDA). Two simple kinetic models, the pseudo-first-order equation and pseudo-second-order equation, were employed to stimulate the kinetic behaviors of adsorption and desorption. The adsorption capacities (q_e) estimated by the pseudo-first-order equation are more accurate in comparison with those simulated by the pseudo-second-order equation. The values of q_e after CADOs are consistent with the predicted results via the previous work, showing that the adsorption behavior and the characteristics of the regenerated adsorbent in altered.

Vellaichamy and Palanivelu⁴⁴ carried out preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid phase extraction on to MWCNTS impregnated with D₂EHPA-Topo mixture. A solid phase extraction method has been developed for the determination of copper, nickel and zinc ions in natural water samples. This method is based on the adsorption of copper, nickel and zinc on multiwalled carbon nanotubes (MWCNTs) impregnated with di-(2-ethyl hexyl phosphoric acid) (D₂EHPA) and tri-n-octyl phosphine oxide (TOPO). The developed method was applied for the determination of copper, nickel and zinc in electroplating wastewater and real water sample with satisfactory results (R.S.D.'s <10%). Allah and Deraz⁴⁵ studied catalytic oxidation of carbon monoxide on non-doped and zinc oxide doped nickel alumina catalyst. Alumina-supported NiO catalysts, promoted with 0.14-3 wt.% ZnO, were prepared by impregnation and then calcined at 400, 600, and 800°C for 4 and 40 h. The phase analysis, surface and catalytic properties were investigated by using XRD technique, nitrogen adsorption at -196°C, and oxidation of CO by O₂ at 200-300°C, respectively. The maximum increase in the catalytic reaction rate constant per unit surface area measured at 250°C due to doping with 3 wt.% ZnO attained 78 and 217% for the catalysts calcined at 400 and 600°C for 4 h, respectively. Bayat⁴⁶ made a comparative study of adsorption properties of Turkish fly ashes 1 case of nickel (II), copper (II) and zinc (II). The objective of this study was to compare two different Turkish fly ashes (Afsin-Elbistan and Seyitomer) for their ability to remove nickel, copper and zinc from an aqueous solution. The effect of contact time, pH, initial metal concentration and fly ash origin on the adsorption process at 20 ± 2°C were studied. The effectiveness of fly ash as an adsorbent improved with increasing calcium (CaO) content. Adsorption data in the range of pH values (3.0-8.0) using Ni (II) and Cu (II) concentrations of 25 ± 2 mg/L and Zn(II) concentration of 30 ± 2 mg/L in solution were correlated using the linear forms of the Langmuir and Freundlich equations.

In the experiments of desorbing copper ions. Zhang et al.⁵⁶ worked on preparation and evaluation of a novel Fe-Mn binary oxide adsorbent for effective arsenite removal.

Arsenite As (III) is more toxic and more difficult to remove from water than arsenate As (V). As there is no simple treatment for the efficient removal of As(III), an oxidation step is always necessary to achieve higher removal. The adsorbent was characterized by BET surface areas measurement, powder XRD, SEM, and XPS. The results showed that prepared Fe–Mn binary oxide with a high surface area was amorphous. The results compared favorably with those obtained using other adsorbent. The effects of anions such as humic acid (HA), which possibly exist in natural water, on As(III) removal were also investigated. The high uptake capability of the Fe–Mn binary oxide makes it potentially attractive adsorbent for the removal of As (III) from aqueous solution. Mahmoud et al.⁴⁸ produced removal and preconcentrators of lead (II), copper (II), chromium (III) and iron (III) from waste waters by surface developed alumina adsorbents with immobilized 1-nitroso-2-naphthol. The potential removal and preconcentration of lead (II), copper (II), chromium (III) and iron (III) from wastewaters were investigated and explored. Three new alumina adsorbent of acidic, neutral and basic nature (I-III) were synthesized via physical adsorption and surface loading of 1-nitroso-2-naphthol as a possible chelating ion-exchanger. The outlined results from the distribution coefficient and separation factor evaluations (low metal ion concentration levels) were found to denote a different selectivity order: Pb (II) > Cu (II) > Cr (III) due to the strong contribution of alumina matrix in the metal binding processes. Ren et al.⁴⁹ utilized adsorptive removal of arsenic from water by an iron – zirconium binary oxide adsorbent arsenate and arsenite may exist simultaneously in groundwater and led to a greater risk to human health. In this study, an iron-zirconium (Fe-Zr) binary oxide adsorbent for both arsenate and arsenite removal was prepared by a coprecipitation method. The ionic strength effect experiment, measurement of zeta potential, and FTIR study indicate that As (V) forms inner-sphere surface complexes, while As(III) forms both inner- and outer-sphere surface complexes at the water/Fe-Zr binary oxide interface.

Chen et al. evaluated Characterization of carbonated tricalcium silicate and its sorption capacity for heavy metals: A micron scale composite adsorbent of active silicate gel and calcite. Adsorption- based processes are widely used in the treatment of dilute metal-bearing wastewaters. The development of versatile, low-cost adsorbents is the subject of continuing interest. The effects of metal ion concentration, pH and contact time on binding ability was investigated by kinetic and equilibrium adsorption isotherm studies. The adsorption capacity for Pb (II), Cr (III), Zn (II) and Cu (II) was found to be 94.4 mg/g, 83.0 mg/g, 52.1 mg/g and 31.4 mg/g, respectively.

Mahmoud et al.⁶² analyzed the removal and preconcentration of Pb (II) from drinking tap water and wastewater samples via applications of newly modified three alumina

physically loaded-dithizone adsorbents. Selective removal of Pb (II) from wastewater samples was accomplished with percentage recovery values of 94-99 + 1-2%, while the results collected from the selective preconcentration of Pb (II) from drinking tap water proved excellent percentage recovery values of 96-99 + 2-3% and 94-95 + 2-4% for the two studied concentration values 1.212 ng mL and 4.800 g/mL, respectively. Sun et al.¹⁰ discussed characterization of adsorbent composition in co-removal of hexavalent chromium with copper precipitation. Mechanisms of hexavalent chromium co-removal with copper precipitation by dosing Na₂CO₃ were studied with a series of well-designed batch tests using solutions containing 150 mg L⁻¹ Cu (II) and 60 mg L⁻¹ Cr (VI). solubility products, neither copper carbonate nor copper hydroxide precipitates can be produced at pH around 5.0 for a pure 150 mg L⁻¹ copper precipitation. Characterization of copper carbonate precipitates (adsorbent) was carried out through developing pC-pH curves of the systems by both equilibrium calculations and MINEQL⁺ 4.5 (a chemical equilibrium modeling software). Li et al.⁵⁰ synthesized preparation of macroporous bead adsorbents based on poly(vinyl alcohol) chitosan and studied their adsorption properties for heavy metals from aqueous solution. A novel macroporous bead adsorbents based on poly(vinyl alcohol)/chitosan (PVA/CS beads) were prepared, characterized and were used for the adsorption of heavy metal ions from aqueous solution. The resulting PVA/CS beads were perfectly spherical in shape and exhibited good mechanical strength and chemical stability. The presence of NaNO₃ (0-0.137 mol/L) had little effect on Cu²⁺ adsorption, but the adsorption of Pb²⁺, Zn²⁺ and Cd²⁺ decreased significantly in the same conditions. Various thermodynamic parameters were calculated and the results showed that the adsorption of all metal ions onto PVA/CS beads was feasible and endothermic in nature. The results from the sequential adsorption-desorption cycles showed that PVA/CS bead adsorbents held good desorption and reusability, which would be a potential application in the fixed-bed continuous-flow column for the removal of heavy metals. Wei et al.⁵¹ used selective adsorption and separation of chromium (VI) on the magnetic iron-nickel oxide from waste nickel liquid. A new composite adsorbent, iron oxide coated zeolite (IOCZ), was characterized and employed for the removal of Cu(II) from aqueous solution using fixed bed column. Scanning electron microscope (SEM), FTIR, X-ray diffraction spectrum (XRD) and BET analyses were used to study the surface properties of the coated layer. The Thomas model was found suitable for the description of breakthrough curve at all experimental conditions, while Adams-Bohart model was only for an initial part of dynamic behavior of the IOCZ column. The theoretical breakthrough curve profile in the dynamic process. The saturated column was regenerated by 1 mol⁻¹ hydrogen chloride solution and IOCZ could be reused in Cu(II) removal.

Wu et al.⁵² carried out chromium removal by confining the magnetic properties of iron oxide with adsorbents properties of carbon nanotubes. The adsorption behaviors of

lanthanum (III) from an aqueous chloride medium, using iron oxide loaded calcium alginate beads were studied using equilibrium batch and column flow techniques. The effect of pH, contents of loaded iron oxide, ionic strength, adsorbent dose, contact time, and temperature on adsorption capacity of the magnetic beads was investigated. The Langmuir adsorption isotherm models were used for the description of the adsorption process. Furthermore, column breakthrough curves were obtained and the La (III) loaded magnetic beads were regenerated using 0.05 mol/L CaCl_2 solution. Gupta et al.⁵³ studied lanthanum adsorption using iron oxide loaded calcium alginate beds. The adsorption features of multiwall carbon nanotubes (MWCNTs) with the magnetic properties of iron oxides have been combined in a composite to produce a magnetic adsorbent. Composites of MWCNT/nano-iron oxide were prepared, and characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and Fourier transform infrared spectroscopy (FTIR). The composites have demonstrated a superior adsorption capability to that of activated carbon. The results also showed that the adsorptions of Cr (III) on the composites is strongly dependent on contact time. Streat et al.⁵⁴ discovered hydrous ferric oxide as an adsorbent in water treatment. Freshly prepared granular ferric hydroxide using both a freeze/thaw and ambient temperature synthesis route are compared with a commercially available product for the adsorption of trace arsenic from water. The effect of interfering anions is discussed in relation to the adsorption isotherms in the pH range 4-9. Also, breakthrough curves are examined to show the effect of anionic interference in packed column operation.

Mahmoodi et al.⁵⁵ worked on magnetic ferrite nanoparticle–alginate composite. Magnetic ferrite nanoparticle (nickel–zinc ferrite) (MFN)–alginate composite was synthesized and characterized. Dye removal ability of MFN–alginate from single and binary systems was studied. The effect of MFN–alginate dosage and pH on dye removal was elucidated. The dye adsorption isotherm and kinetics were studied. It was found that BB9, BB41 and BR18 followed the Tempkin, Langmuir, and Langmuir isotherms, respectively. Wang et al.⁵⁶ studied adsorption capability for Congo red on nanocrystalline MFe_2O_4 (M = Mn, Fe, Co, Ni) spinel ferrites. It is the first time to give a comprehensive comparison and analysis of the adsorption capacity of ferrite nanocrystals with spinel structure for Congo red has been studied. Research indicates that the cations distribution of MFe_2O_4 ferrites is the most important factor to decide their adsorption capacity. Electrostatic absorption was conceived as the main adsorption mechanism. Meanwhile, the MFe_2O_4 nanoparticles exhibited a clearly ferromagnetic behavior under applied magnetic field, which allowed their high-efficient magnetic separation from wastewater. Aziz et al.⁵⁷ enhanced magnetic separation and photocatalytic activity of nitrogen doped titania photocatalyst supported on strontium ferrite. The synthesized catalysts were further characterized with X-ray diffraction (XRD), transmission electron microscope (TEM),

energy dispersive X-ray spectroscopy (EDS), BET surface area analysis, vibrating sample magnetometer (VSM), X-ray photon spectroscopy (XPS) and visible light spectroscopy analysis for their respective properties. It also resulted in reduced band gap (2.8 eV) and better visible light absorption between 400 and 800 nm compared to N-doped TiO₂. The photocatalytic activity was investigated with a recalcitrant phenolic compound namely 2,4-dichlorophenol (2,4-DCP) as a model pollutant under direct bright and diffuse sunlight exposure. A complete degradation of 2, 4-DCP was achieved with an initial concentration of 50 mg/L for both photocatalysts in 180 min and 270 min, respectively under bright sunlight. Similarly, the diffuse sunlight study resulted in complete degradation for supported N-TiO₂ and > 85% degradation N-TiO₂, respectively. Safarik⁵⁸ magnetically modified microbial cells is a new type of magnetic adsorbents. Microbial cells, either in free or immobilized form, can be used for the preconcentration or removal of metal ions, organic and inorganic xenobiotics or biologically active compounds. Magnetic modification of these cells enables to prepare magnetic adsorbents that can be easily manipulated in difficult-to-handle samples, such as suspensions, in the presence of external magnetic field.

REFERENCES

1. C. Noguera, *Physics and Chemistry at Oxide Surfaces*, Cambridge University Press: Cambridge, U.K. (1996).
2. H. H. Kung, *Transition Metal, Oxides: Surfaces Chemistry and Catalysis*, Elsevier; Amsterdam (1989).
3. V. E. Henrich and P. A. Cox, *The Surface Chemistry of Metal Oxides*, Cambridge University Press, Cambridge UK (1994).
4. A. F. Wells, *Structural Inorganic Chemistry* 6th Ed., Oxford University Press, New York (1987).
5. J. A. Rodriguez and M. G. Fernandez, *Synthesis, Properties and Applications of Oxide Nanoparticles* Wiley : New Jersey (2007).
6. M. G. Fernandez, A. A. Martinzes, J. C. Hanson and J. A. Rodriguez, *Chem. Revs.*, **104**, 4063 (2004).
7. Q. Qian, K. Mochidzuki, T. Fuji and A. Sakoda, *J. Hazard. Mater.*, **172**, 1137-1144 (2009).
8. A. K. Arora and Ritu, S. Devi, *Curr. Trends Biotechnol. Chem. Res.*, **2(1)**, 52-56 (2012).

9. Q. Chen, C. D. Hills, M. Yuan, H. Liv and M. Tyrer, *J. Hazard. Mater.*, **153**, 775-783 (2008).
10. J. M. Sun, X. H. Zhao and J. C. Huang, *Chemosphere*, **58**, 1003-1010 (2005).
11. A. K. Arora, Ritu and P. Kumar, *Asian J. Chem.*, **25(13)**, 7283-7386 (2013).
12. W. Turbeville and N. Yap, *Catal. Today*, **116**, 519-552 (2006).
13. A. K. Arora and Ritu, *Int. J. Chem. Sci.*, **11(3)**, 1335-1341 (2013).
14. M. E Mahmoud, M. M. Osman, O. S. Hafez, A. H. Hegazi and E. Elmelegy, *Desalination*, **251**, 123-130 (2010).
15. A. K. Arora and Ritu, *Int. J. Chem.*, **11(3)**, 1342-1352 (2013).
16. A. K. Arora and Ritu, *Int. J. Chem. Sci.*, **11(3)**, 1353-1362 (2013).
17. A. K. Arora and Ritu, *Res. J. Chem. Sci.*, **3(8)**, 18-28 (2013).
18. A. K. Arora, M. Sharma, V. S. Jaswal and P. Kumar, *J. Nanotechnol.*, **7** (2014).
19. V. S. Jaswal, A. K. Arora J. Singh, M. Kinger and V. D. Gupta, *Oriental J. Chem.*, **30(2)**, 559-566 (2014). doi
20. A. K. Arora, S. Devi, V. S. Jaswal, J. Singh, M. Kinger and V. D. Gupta, *Oriental J. Chem.*, **30(04)**, 1671-1679 (2014).
21. A. K. Arora, V. S. Jaswal, K. Singh and R. Singh, *Oriental J. Chem.*, **32(04)** (2016) (In Press).
22. Q. Qian, K. Mochizuki, T. Fuji and A. Sakoda, *J. Hazard. Mater.*, **172**, 1137-1144 (2009).
23. X. Wang, Q. Chen, Z. Yin, P. Zhang, Z. Long and Z. Su, *Hydrometallurgy*, **69**, 39-44 (2003).
24. H. F. Garces, H. M. Galindo, L. J. Garees, J. Hunt, A. Morey and S. L. Suib, *Microporous and Mesoporous Materials*, **127**, 190-197 (2010).
25. S. Kolboe, *J. Catal.*, **113**, 199-207 (1969).
26. K. O. Asare and D. W. Fuerstenav, *Int. J. Mineral Process.*, **6**, 85-104 (1979).
27. K.O. Asare and D.w. Fuerstenav, *Int. J. Mineral Process.*, **7**, 219-234 (1980).
28. P. Ning, H. Yi, Q. Yu, X. Tang, L. Yang and Z. Ye, *J. Rare Earths*, **28**, 581-586 (2010).
29. P. Bose, M. Bose and S. Kumar, *Adv. Environ. Res.*, **7**, 179-195 (2002).

30. S. C. Pan, C. C. Lin and D. H. T. Seng, *Resour. Conserv. Recycl.*, **39**, 79-90 (2003).
31. M. Arias, C. Novo, E. Lopez and B. Soto, *Geoderma*, **133**, 151-159 (2006).
32. W. Turbeville and N. Yap, *Catal. Today*, **116**, 519-525 (2006).
33. N. Turan, S. Eleveli and B. Mesci, *Appl. Day Sci.*, **52**, 392-399 (2011).
34. X. Li, Y. Tang, X. Cao, D. Lu, F. Luo and W. Shao, *Colloid Surfaces A*, **317**, 512-521 (2008).
35. K. Polychronopoulou, F. C > Galisteo, M. L. Granados, J. L. G. Flerro, T. Bakas and A. M. Efstathiou, *J. Catal.*, **236**, 205-220 (2005).
36. R. Han, L. Zou, X. Zhao, Y. Xu, F. Xu, Y. Li and Wang, *Chem. Engg. J.*, **149**, 123-131 (2009).
37. N. Chen, Z. Zhang, C. Fing, D. Zhu, Y. Yang and N. Sugiura, *J. Hazard. Mater.*, **186**, 863-868 (2011).
38. E. A. Deliyanni, E. N. Peleka and K. A. Matis, *J. Hazard. Mater.*, **172**, 550-558 (2009).
39. K. P. Wang, J. L. G. Fierro and A. M. Efstathious, *Appl. Catal. B: Environ.*, **57**, 125-137 (2005).
40. A. K. Arora and Kamaluddin, *Colloid Surfaces A*, **298(3)**, 186-191 (2007).
41. A. K. Arora, V. Tomar, Aarti, K. T. Venkateswararao and Kamaluddin, *Int. J. Astrobiol.*, **6(4)**, 267-271 (2007).
42. A. K. Arora and Kamaluddin, *Astrobiol.*, **9(2)**, 165-171 (2009).
43. J. Y. Tseng, C. Y. Chang, C. F. Chang, Y. H. Chen, C. C. Chang, Dr. Ji, C. Y. Chiv and P. C. Chiang, *J. Hazard. Mater.*, **171**, 370-377 (2009).
44. S. Vellaichamy and K. Palanivelu, *J. Hazard. Mater.*, **185**, 1131-1139 (2011).
45. N. Allah and M. Deraz, *Colloid Surfaces A*, **218**, 213-223 (2003).
46. B. Bayat, *J. Hazard. Mater.*, **95**, 251-273 (2002).
47. G. Zhang, J. Qu, H. Liv, R. Liv and R. Wu, *Water Res.*, **41**, 1921-1928 (2007).
48. M. F. Mohmaud, M. M. Osman, O. S. Hafez and E. Elmelegy, *J. Hazard. Mater.*, **173**, 349-357 (2010).
49. Z. Ren, G. Zhang and J. P. Chen, *J. Coll. Interface Sci.*, **358**, 230-237 (2011).
50. J. M. Li, X. H. Zhao and J. C. Huang, *Chemosphere*, **58**, 1010-1015 (2005).

51. L. Wei, G. Yang, R. Wang and W. Ma, *J. Hazard. Mater.*, **164**, 1159-1163 (2009).
52. D. Wu, J. Zhao, L. Zhang, Q. Wu and Y. Yang, *Hydrometallurgy*, **101**, 76-83 (2007).
53. V. K. Gupta, S. Agarwal and T. A. Saleh, *Water Research*, **45**, 2207-2212 (2011).
54. M. Streat, K. Heligardt and N. L. R. Newton, *Process Safety Environ. Prot.*, **86**, 21-30 (2008).
55. N. M. Mahmoodi, *J. Taiwan Inst. Chem. Eng.*, **44**, 322-330 (2013).
56. L. Wang, J. Li, Y. Wang, L. Zhao and Q. Jiang, *Chem. Engg. J.*, **181-182**, 72-79 (2012).
57. A. A. Aziz, K. S. Yong, S. Ibrahim and S. Pichiah, *J. Hazard. Mater.*, **199-200**, 143-150 (2012).
58. I. Safarik and M. Safarikova, *China Patricuology*, **5**, 19-25 (2007).

Revised : 03.09.2016

Accepted : 07.09.2016