The Role of Transition Metal Oxides as effective Adsorbent

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ABSTRACT:

The Transition metal oxides / mixed metal oxides have various applications as catalyst, photocatalyst, sensors, superconductors, adsorbent, ceramics, fuels, antifungal agents and have large number of applications in medicines. These transition metal / mixed metal oxides play a very important role in day to day human life. Today transition metal oxides are attracting special attention of scientists due to their easy mode of formation and multifunctional behavior. In this paper an attempt has been made to focus on their applications as Adsorbent in various chemical reactions.

Keywords: Transition Metal oxides, Mixed metal oxides, chemical reactions, Adsorbent

INTRODUCTION:

The transition metals have the special properties of formation of colored compounds and show magnetic properties. Metals of d-block elements are used for many industrial applications. They behave as catalysts, super conducting materials, sensors, ceramics, phosphors, crystalline lasers etc. The transition metals and their compounds are used as catalysts is chemical industry and in battery industries. Besides, these compounds can be used in formation of interstitial compounds and alloy formation Besides these they are excellent photoactive materials and work as photosensitizer. Mixed metal oxide (MMO) electrodes are devices with useful properties for chemical electrolysis. The term refers to electrodes in which the surface contains two kinds of metal oxides- one kind usually RuO_2 and IrO_2 desired reaction such as production of chlorine gas. The other metal oxides is typically titanium dioxide which does not conduct or catalyze the reaction, but is cheaper and prevents corrosion of the interior. The interior of the electrode is typically made of titanium. The amount of precious metal (that is other than titanium) can be around 10 to 12 grams per square meter. Fe and O form a number of phases, e.g., FeO (wustite); Fe_3O_4 (magnetite), Fe_2O_3 (hematite), Fe_2O_3 (maghemite). The latter phase is synthetic while remaining oxides occur in nature. The Fe-O phase diagram shows the predominance of the Fe_2O_3stoichiometry for most temperature and pressure preparation conditions [1]. The magnetic properties of the Fe oxides have been extensively studied; in particular, the enhancing magnetic recording properties of magnetic and maghemite for nanostructure materials, or the use of the latter in Fe_2O_3-SiO_2 composite materials having magneto- optical properties. Most physio-chemical studies are centered in the alpha (corundum structure with a distorted hexagonal anion closed – packed) and gamma (cubic inverse spinel) phases. Size stability of the polymorphs has been studied but there is still a lack of consensus in a significant number of issues; particularly related to the existence of Nano-particles with alpha structure.

Adsorbents:

Ariass et al. [2] investigate Competitive adsorption and desorption of copper and zinc in acid soils As an aid to evaluating the environmental threat passed by Cu and Zn when both are present in acids 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. These data were better fitted by the Freundlich equation than by he Langmuir equation. Qian et al. [3] found that 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 N2adsorption, XRD, SEM, EDX, pH determination and elemental analysis. 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 high copper removal ability of the MFS-derived materials is attributed to their intermediate surface area, strong surface basicity and the presence of iron (hydro) oxides on their surface. The adsorbent can be applied to remove copper from water or soil by fixation onto the surface. Characterization and properties of iron oxide coated zeolite as adsorbent [4] 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 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 was compared with experimental 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. Han et al. [5] examined reuse of waste silica as adsorbent for metal removal by iron oxide modification. Silica gel is widely used in research laboratories, especially for the purification of organic compounds. Consequently, waste silica gel is generated in increasing amounts. In the preparation of the adsorbent, the optimal pretreatment temperature and iron concentration were investigated. The coated waste silica was characterized for BET surface area, pore size, specific pore volume and iron content. Iron oxide- coated waste silica was tested for the adsorption of Pb(II), Cu((II) and Ni(II) from solutions in a batch system. The presence of salt reduced the adsorption efficiency of the adsorbent. The adsorption behavior followed both Langmuir and Freundlich isotherms (250C).Tseng et al. [6] reviewed kinetics and equilibrium of disorder removal of copper from magnetic polymer adsorbent. Their 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 ethylenediaminetetraacetic acid (EDTA). Stage-wise 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 simulate the kinetic behaviors of adsorption and desorption. With respect to the kinetics of adsorption behavior, the simulated results by both kinetic models exhibit good agreement with the experimental data. The values of qe after CADOs are consistent with the predicted results via the previous work, evidencing that the adsorption behavior and the characteristics of the regenerated adsorbent of D-M-PVAC-IDA were not altered. In the experiments of desorbing copper ions. Zhang et al. [7] worked 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 compare favorably with those obtained using another 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. [8] produced Removal and preconcentrates 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 adsorbents 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 to 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. [9] utilized Adsorptive removal of arsenic from water by an iron – zirconium binary oxide adsorbent Arsenate and arenite may exist simultaneously in groundwater and have led to a greater risk to human health. In this study, an iron-zirconium (Fe-Zr) binary oxide adsorbent for both arsenate and arsenate 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. Han et al. [10] characterized 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 effects of various experimental conditions, such as the flow rate, initial metal concentration and bed depth, were studied. The dynamics of the adsorption process were fitted by Adams–Bohart model and Thomas model. The theoretical breakthrough curve was compared with experimental breakthrough curve profile in the dynamic process. The saturated column was regenerated by 1 mol l−1hydrogen chloride solution and IOCZ could be reused in Cu(II) removal. Chen et al. [11] 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.Wayne Turbeville and Nora Yap checked [12] the chemistry of copper containing Sulphur adsorbents in the presence of mercaptans. A brief review of the chemistry of copper and thiols is given and a contrast is made of the behavior of copper – containing adsorbents used for the desulfurization of liquid hydrocarbon streams that are routinely treated in refinery processes. In addition, it is shown that bulk copper is involved in the adsorption of mercaptans, as there is significantly more sulfur than there is copper on the surface. Reaction mechanisms are proposed for the process of desulfurization of liquid hydrocarbon streams containing mercaptans when using a copper – containing adsorbent.Mahmoud et al. [13] 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-1 and 4.800 ng ml-1, respectively.Mei Sun et al.[14] 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 Na_2CO_3 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. [15] synthesized Preparation of microporous bead adsorbents based on poly (Vinyl alcohol) Chitosan and their adsorption properties for heavy metals from aqueous solution. A novel microporous 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 $NaNO_3$ (0–0.137 mol/L) had little effect on Cu^{2+} adsorption, but the adsorption of Pb^{2+}, Zn^{2+} and Cd^{2+} 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. [16] used Selective adsorption and separation of Chromium (VI) on the magnetic iron – nickel oxide form 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. Deliyanni et al. [17] prepared Modeling the sorption of metal ions from aqueous solution by iron-based adsorbents. The possibility of using iron-based adsorbents (i.e. akageneite or goethite) to remove heavy metal ions from aqueous solutions was the aim of the present review paper. The removal efficiency of the packed-bed column was examined and compared. 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. Dinesh. Mohan and Charies V. Pi Hman Jr. showed activated carbons and low-cost adsorbents for remediation of tri-and hexavalent chromium from water. Hexavalent chromium is a well – known highly toxic metal, considered a priority pollutant. Industrial sources of Cr (VI) include leather training, cooling tower blowdown, plating, electroplating, anodizing baths, rinse waters, etc. The most common method applied for chromate control is reduction of Cr (VI) to its trivalent from in sold (pH) and subsequent hydroxide precipitation of Cr (III) by increasing the pH to 9.0-10-0 using lime.After an overview of chromium contamination is provided, more than 300 papers on chromium remediation using adsorption are discussed to provide recent information about the most widely used adsorbents applied for chromium remediation. Wu et al. [18] was 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 CaCl2 solution. V.K. Gupta et al. [19] 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 were 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 show that the adsorptions of Cr (III) on the composites is strongly dependent on contact time.M. Streat et al. [20] discoveredHydrous ferric oxide as an adsorbent in water treatment: Batch and mini column adsorption of arsenic phosphorous fluorine and cadmium ions 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. Bayat et al.[21] developed Comparative study of adsorption properties of Turkishesin fly ashes. The 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 [Ni(II)], copper [Cu(II)] and zinc [Zn(II)] from an aqueous solution. 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 Freudlich equations. S. Vellaichamy and K. Palanivelu [22] Investigated Preconcentration and separation of copper, nickel and zinc in aqueous samples by flame atomic absorption spectrometry after column solid phase extraction onto 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%).Mahmoodi et al. [23] 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 Temkin, Langmuir, and Langmuir isotherms, respectively. Wang et al. [24]Adsorption capability for Congo red on nanocrystalline MFe2O4(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 CR. Research indicates that the cations distribution of MFe2O4 ferrites is the most important factor to decide their adsorption capacity. Electrostatic absorption was conceived as the main adsorption mechanism. Meanwhile, the MFe2O4 nanoparticles exhibited a clearly ferromagnetic behavior under applied magnetic field, which allowed their high-efficient magnetic separation from wastewater.Aziz et al. [25]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.Safarik[26]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.

CONCLUSION:

Above mentioned literature shows wide applications of transition metal /mixed metal oxides as adsorbent in various reactions like Hydrous ferric oxide as an adsorbent in water treatment: Batch and mini column adsorption of arsenic phosphorous fluorine and cadmium ions 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. Comparative study of adsorption properties of Turkish sin fly ashes So, transition metal/mixed metal oxides have broad applications as adsorbent in various chemical reactions.

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