

Assessment of Heavy Metals Removal by Binary and Ternary Mixed Oxide Nanocomposites

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Abstract: The potential of various binary and ternary mixed oxide nanocomposites for the removal of heavy metals from contaminated water has been reviewed. Various conventional methods for heavy metal removal such as precipitation, evaporation, electroplating and also ion exchange have been applied since previous years. However, these methods have several disadvantages such as only limited to certain concentrations of metals ions, generation, large amount of toxic sludge and the capital costs are much too high to be economical. Hence, adsorption using binary and ternary mixed oxide nanocomposite is found to be more environmentally friendly. High adsorption capacities, cost effectiveness and their abundance in nature are the important parameters which explain why the adsorbent is economical for heavy metal removal. In this review, a list of adsorbent literature has been compiled to provide a summary of available information on a wide range of binary and ternary mixed oxide nanocomposites for removing heavy metals from contaminated water.

Keywords: Heavy metals, Preconcentration, Binary oxide, Ternary oxide, Nanocomposites.

1. INTRODUCTION

Water pollution raises a great concern nowadays since water constitutes a basic necessity in life and thus, is essential to all living things. The fast-paced development of industries such as metal mining operations, fertilizers and paper industries and pesticides have deliberately discharged various types of pollutants into the environment especially in developing countries. The presence of various pollutants such as industrial effluents, mining and agricultural wastes, sewage and domestic wastes are continuously discharged into the water system and further affecting our ecosystem due to their lethal effects. Among other issues, water contaminations by heavy metals are more pronounced than other pollutants especially when heavy metals are exposed to the natural ecosystem. 'Heavy metals' refers to any elements with the atomic weights between 63.5 and 200.6 and a specific gravity greater than 5.0 [Srivastava and Majumder, 2008]. Cadmium, zinc, copper, uranium, lead, mercury and chromium, are some examples of heavy metals which originate from activities of metal plating, mining, battery manufacture, petroleum refining and paint manufacturing (Williams *et al*, 1998).

Heavy metals are non-biodegradable pollutants and they are very difficult to eliminate naturally from the environment. Almost all heavy metal elements are highly toxic when their concentration exceeds their permissible limit in the ecosystem. High concentration of heavy metals may accumulate in the human body once they interrupt in human food chain and possibly in effect, cause severe health problems if the metals exceed the permitted concentration [(Babel and Kurniawan, 2004). Zinc is one of trace elements essential for human health especially to protect against premature aging of the skin and muscles of the body but too much zinc can cause eminent health problems, such as stomach cramps, skin irritations, vomiting, nausea and anemia (Oyaro *et al*, 2007). Excessive intake of chromium by humans leads to hepatic and renal damages, capillary damage, gastrointestinal irritation and central nervous system irritation (Wan Ngah *et al*, 2008). Lead has its environmental importance due to its widely known toxicity especially in industries such as storage-battery manufacturing, printing, fuel combustion and also photographic materials (Carson *et al*, 1986).

Generally, all these treatments lead to certain disadvantages such as incomplete removal of heavy metals, high-energy requirements and production of toxic sludge (Eccles, 1999). Numerous approaches have been studied for the development of more effective methods in removing metal pollution and the adsorption process is found to be more practicable over other techniques. Adsorption process is one of the easiest, safest and more cost-effective methods for heavy metal removal from industrial effluents (Rahmani *et al.*, 2009) and this process is already established as a simple operation and an easy-handling process (Sharma *et al.*, 2009).

Extensive studies have been undertaken in recent years with the aims of finding an alternative in the form of economic adsorbents for water treatment. Various binary and ternary mixed oxide nanocomposites have been utilized as adsorbents for the adsorption process due to their potential adsorption capacities. In this work, the adsorption process using mixed oxide adsorbents for heavy metal removal from different sources is presented by highlighting the applicability of adsorbents, optimum parameter and adsorption capacity. The main objective of this review is to provide a summary of information concerning the adsorption process using mixed oxides as adsorbents for heavy metal removal.

Toxicity and Sources of Heavy Metals in Waste Water

Heavy metals are a natural constituent on earth commonly known with properties such as having persistence, high toxicity and also serving as non-biodegradable pollutants when they accumulate in the ecosystem. Source of heavy metals that penetrate into the water system can derive from both natural and anthropogenic sources. The main source of heavy metal contamination involves urban industrial aerosols, solid wastes from animals, mining activities, also industrial and agricultural chemicals. Sometimes most heavy metals contaminate the water system through the various industrial activities or even from acid rain which breaks down the soils and rocks, releasing heavy metals into water resources (Alluri *et al.*, 2007). Table 1 summarizes the variety of sources of heavy metal that exist in the environment (Alluri *et al.*, 2007) and the limits on the types and concentration of heavy metals that may be present in the discharged wastewater can be referred to the MCL(Maximum Contaminant Level) standards established by the USEPA (Babel and Kurniawan, 2003).

The presence of heavy metals in the environment leads to a growing number of environmental problems such as the deterioration of several ecosystems due to its persistent accumulation. For instance, nickel is one of the carcinogenic elements which cause serious lung and kidney problems, aside from gastrointestinal distress, pulmonary fibrosis and skin dermatitis if exceeding its critical level (Borba *et al.*, 2006). Instead of nickel, lead might also cause damage to the kidney, liver and reproductive system. The toxic symptoms of nickel are anemia, insomnia, headache, dizziness, irritability, weakness of muscles, hallucination and renal damages (Naseem and Tahir, 2001). The emission of heavy metals into the environment from mining operations (Nriagu, 1989) will pollute the surface and also underground water sources. This may lead to soil pollution and the increasing rate of pollution when mined ores are dumped on the ground surface for manual dressing (Garbarino *et al.*, 1955). When agricultural soils are polluted, these metals are taken up by plants and consequently accumulate in their tissues (Trueby, 2003). Animals that graze on such contaminated plants and drink from polluted waters, as well as marine lives that breed in heavy metal polluted waters also accumulate such metals in their tissues and milk, if lactating (Horsfall and Spiff, 1999). All this acquire established wastewater regulations to minimize the human and environmental exposure to hazardous heavy metals.

Table 1: Various sources of heavy metal into the environment (Babel and Kurniawan, 2003; Alluri *et al.*, 2007)

Heavy metal	Sources of heavy metals	Toxicities	MCL (mg/L)
Cadmium	Welding, electroplating, pesticide fertilizer, Cd-Ni batteries	Kidney damage, renal disorder, human carcinogen	0.01
Lead	Paint, pesticide, smoking, automobil emission, mining, burning of coal	Damage the fetal brain, diseases of the kidneys, circulatory system and nervous system	0.06
chromium	metallurgy, electroplating, leather tanning, textile dyeing, paint, ink and aluminum manufacturing industries	Carcinogenic to both humans and animals. Gastric pain, nausea and vomiting, severe diarrhea.	0.05
uranium	Mining, uranium ore, nuclear weapons manufacturing.	carcinogenic for human, Kidney damage, liver damage	0.05

Zinc	refineries, brass manufacture, metal plating, plumbing	Depression, lethargy, neurological signs and increased thirst	0.80
Mercury	Pesticides, batteries and paper industry	Rheumatoid arthritis, diseases of the kidneys, circulatory system and nervous system	0.00003

Heavy Metal Removal Techniques

Different techniques are used for the separation and preconcentration of metals in a solution. These methods, however, have not enough sensitivity and selectivity to establish the heavy metal amounts of real solution without using a preconcentration step. A preconcentration step be able not only concentrate the analyte but also simplify the matrix of the sample that is usually strongly desired. These include liquid-liquid extraction, precipitation, ion exchange, cloud point extraction and solid phase extraction. These have been used for the separation and enrichment of trace amounts of heavy metals from aqueous solutions. However, disadvantages such as significant chemical additives, solvent losses, complex equipment, large secondary wastes, pre filtration problems and time consuming procedures, limit the application of most of these techniques (Chang *et al.*, 2009).

Table 2: Methods for heavy metal removals (Oconnell *et al.*, 2008)

Separation Technique	Advantages	Disadvantages
liquid-liquid extraction		Solvent losses, complex equipment, time consuming procedures
Chemical precipitation	Simple operation, Non-metal selective, Inexpensive cost	Large production of sludge, High cost of disposal sludge
Membrane filtration	Less production of solid waste, Low chemical consumption	High initial capital and maintenance cost
Electrochemical treatment	Metal selective Potential treat effluent > 2000 mg/ dm ³	High initial capital cost
Adsorption	High adsorption capacity	Need to dispose of adsorbents.
Ion exchange	Metal selective High regeneration of materials	High initial capital and maintenance cost

Solid Phase Extraction Technique

Solid-phase extraction (SPE) is a sample-pretreatment method for sample enrichment, sample isolation and matrix simplification. It helps not only extract and enrich traces of organic and inorganic compounds from various samples but also remove the interfering components from the complex matrices in order to obtain a cleaner extract containing the analytes of interest (Żwir-Ferenc and Biziuk, 2006). It is usually used to clean up a sample before using a chromatographic or other analytical method to quantify the amount of analyte in the sample.

The principle of SPE is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of partitioning analytes between two immiscible liquid phases, as in LLE, SPE involves partitioning of analytes between a liquid solvent and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent and purification of extract after extraction.

Solid phase extraction is achieved through the interaction of three components: the sorbent, the analyte and the solvent. The analyte must be attracted more strongly to the sorbent than to the matrix. The best solid phase extraction mechanism and procedures are defined by the characteristics of the analyte in the sample (Żwir-Ferenc and Biziuk, 2006).

Sorbent selection depends on the analyte characteristics, the sample matrix and the analytical method. Column selection also depends on the impurities that must be separated from the analyte. If the analytes and stationary phase are polar, normal phase extraction is indicated. When the analytes are less polar, reverse phase separation is advised. The properties of sample impurities can often be exploited in analyte (Sabik *et al.*, 2000).

Adsorption Process

Recently, the adsorption process has gained interest as a more promising method for the long term as it is seen to be a more effective and economic approach for heavy metal removal. Adsorption is a fundamental process today due to its flexibility in design and simple operation instead of having to perform adsorptions that are perceived as impractical by most conventional techniques. The term “adsorption” refers as a mass transfer process by which a substance is transferred from the liquid phase to the surface of a solid and becomes bound by physical and/or chemical interactions (Babel and Kurniawan, 2003). The advantages of the adsorption process in removing or minimizing the heavy metals even at low concentration enhance the application of adsorption as one practical treatment.

Adsorption can be categorized into two; physical adsorption and chemisorption. Physical adsorption is a reversible phenomenon resulting from intermolecular forces of attraction between molecules of the adsorbent and the adsorbate. Meanwhile, chemisorption is a result of the chemical interaction between the solid and the adsorbed substance. It is an irreversible phenomenon and is also called activated adsorption (Yadla *et al.*, 2012). In terms of the temperature, high physical adsorption occurs at a temperature as close to the critical temperature of a given gas while chemical adsorption occurs at temperatures much higher than the critical temperature. Under certain conditions, both processes can occur simultaneously or alternately (Dabrowski, 2001).

Some parameters should be considered during the adsorption process between adsorbent and adsorbate including the physical and chemical characteristics of adsorbent and adsorbate, the concentration of adsorbate in liquid solution, temperature, pH and also contact time (Cheremisinoff and Morresi, 1978). PH is the most important factors than others as pH controls the distribution of charge on the adsorbent surface between the adsorbate ion. However, in most sorption studies point of zero charge (pHZPC) should be considered to be compared with pH as (pHZpc) determines the limitations of the adsorbent's pH. PHZPC is the charge at the solid surface of adsorbent determined by the protonation and deprotonation of adsorbate ions. The surface charge density of surface depends on the specific metal ions which react directly with the adsorbent surface. For instance, when the pH value of solution is higher than pHzpc, the surface charge of the adsorbent will be negatively charged and vice versa (Haghseresht *et al.*, 2003). Otherwise, the increase of pH within a certain limit can increase the adsorption rate (Kumar and Bandyopadhyay, 2006) but further increase in pH can decrease the adsorption rate as certain adsorbate ions in a particular range tends to be unaffected by pH (Lata *et al.*, 2007).

Instead of pH, the adsorbent dose is another factor which influences the adsorption process. Based on assumption, when the adsorbent doses increase, the adsorption rate also increases. However, the adsorption rate can decrease if the adsorbent dose further increases, due to the presence of more occupied active sites when the concentration gradient of the adsorbate is kept constant (Ahmaruzzaman and Sharma, 2005). Higher adsorption rate can be obtained once the temperature increases due to the increase of the surface area and the pore volume of adsorbent (Auta and Hameed, 2011). Initial metal concentration can be the driving force to overcome the mass transfer between the surface of adsorbent and the solution (Arief *et al.*, 2008). The initial metal concentration influences the adsorption rate based on the availability of the specific surface functional groups and the ability of the surface functional groups to bind metal ions (especially at high concentrations). Thus, any parameters influencing the adsorptive capacity of adsorbent should be considered during the adsorption process.

Adsorption Mechanism

Adsorption mechanisms are complicated as no simple theory adequately explains the adsorption of metal ions on the adsorbent surface. Previous studies have reported on the various models that describe the mechanism between the adsorbate and the adsorbent. The Langmuir model and Freundlich models are commonly used to describe the sorption isotherms. Some empirical models of equation are listed in Table 3.

Adsorption Isotherm

Sorption isotherm is used to describe the mechanism of how adsorbate ions interact on the surface of adsorbent. There are several isotherm equations available to analyze the experimental sorption equilibrium parameters, but the well-known adsorption isotherm models used for single solute systems are Langmuir (Langmuir, 1918) and Freundlich isotherms [Freundlich, 1906]. Both adsorption isotherm models are found to be more suitable to describe the relationship between q (quantity adsorbed at equilibrium, mg/g) and C (concentration of adsorbates remained in the bulky solution at the equilibrium, mg/L).

Table 3: Adsorption models of the single-component system

Types of mechanism	Equations	Nomenclature	References
Adsorption isotherms			
i) Langmuir isotherms	$Q_e = q_o \times \frac{bC_e}{1 + bC_e}$	q_e is equilibrium metal sorption capacity, C_e is equilibrium solute conc. in solution, q_o and b are Langmuir constants related to maximum sorption capacity (monolayer capacity) and bonding energy of adsorption	Langmuir (1918)
ii) Freundlich isotherms	$Q_e = K_f C_e^{1/n}$	K_f is a biosorption equilibrium constant, q_e is the sorption capacity, n is a constant indicative of biosorption intensity	Freundlich (1906)

Langmuir Isotherm

Based on Langmuir adsorption theory, molecules are adsorbed at a fixed number of well-defined active sites which are homogeneously distributed over the surface of the adsorbent. These active sites have the same affinity for adsorption of a mono molecular layer and there is no interaction between the adsorbed molecules (Langmuir, 1918).

For Langmuir equation, it is written as:

$$Q_e = q_o \times \frac{bC_e}{1 + bC_e} \quad (1)$$

Where q_e is the metal adsorption capacity of adsorbent and intensively depends on the physical and chemical properties of adsorbate and adsorbent. Langmuir isotherm can be explained based on the assumption; the adsorption process is only limited to mono-layer adsorption and reversible process when no interaction occurs between the molecules adsorbed on the active site and the neighboring sites (Febrianto *et al.*, 2009). This isotherm is suitable for representing chemisorptions on a set of distinct localized adsorption sites (Ruthven, 1984).

Freundlich Isotherm

Freundlich isotherm model interprets the adsorption on heterogeneous surfaces with interactions occurring between the adsorbed molecules and is not restricted to the formation of a monolayer. This isotherm is commonly used to describe the adsorption of organic and inorganic compounds on a wide variety of adsorbents (Febrianto *et al.*, 2009).

For Freundlich equation, it is written as:

$$Q_e = K_f C_e^{1/n} \quad (2)$$

Where K_f is the adsorption equilibrium constant while $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption and C is the equilibrium concentration (mg/L). This model assumes that when the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and, correspondingly, the sorption energy exponentially decreases over the completion of the sorption center of the adsorbent (Faust and Aly, 1987). Langmuir and Freundlich isotherm models are frequently used for describing the short term and mono-component adsorption of metal ions by different materials (Yu *et al.*, 200).

2. DISCUSSION

Removal of Heavy Metals by Binary and Ternary oxides

Multi component sorbents comprising of mixtures of metal oxides and have been shown to be significant in determining the environmental distribution of various contaminants and nutrients. These sorbents form via dissolution, adsorption, co-precipitation, or colloidal interactions and often exhibit different sorption behaviors compared to single component sorbents. With different morphologies and sizes, mixed oxide materials can bring various potential applications into many fields including catalysis and adsorption (Ahmed, 2003).

Investigating the mechanism for the multi-metal-oxides composites and to seek ways to improve the selectivity for interacting with selective species is a necessity. Heavy metals such as Lead and Cadmium may be retained in composite metal oxides by adsorption on surface of iron, manganese and aluminum oxides and hydroxides (Mehmood *et al.*, 2009). Characterization studies of multi component sorbents indicated that the physico-chemical properties of these solids differ significantly from those of their single component constituents. This difference in physico-chemical properties are the primary reason for differences in sorption behavior between multi-component and single component solids.

Binary Mixed Oxide Nanocomposites

Binary mixed oxides are the most significant multi-component sorbents. Binary mixed oxides have high specific surface areas and surface functional groups capable of interacting with both cationic and anionic species (Behrends, 2005). Binary oxides are used in many important processes, and so early research has been driven by the need to understand the performance of various binary oxides in chemical engineering and wastewater treatment as these oxides might be effective adsorbents for metal ion removal (Wang *et al.*, 2004; Zhang *et al.*, 2005; El-Kamash *et al.*, 2007; Fu-wang *et al.*, 2009; Hong *et al.*, 2010; Zhang *et al.*, 2010; Dou *et al.*, 2011). Recently, interest in low-cost, high-surface-area materials, especially binary oxides and their unique applications, such as adsorption and chemical catalysis, has been growing (Koper *et al.*, 1989; Klabunde *et al.*, 1996; Zhu *et al.*, 2008). Several binary oxides have been prepared according to different synthesis methods and characterized (Tee *et al.*, 2005; Lambert *et al.*, 2009). TiO₂-B₂O₃ Nano composite material, Fe-Mn binary oxide adsorbent, iron-zirconium binary oxide adsorbent and nanostructured iron (III)-copper (II) binary oxide are classified as the promising ones for heavy metals removal from aqueous systems.

Nano TiO₂/B₂O₃ Composite Material

Nano B₂O₃/TiO₂ was synthesized from certain amount of boric acid (H₃BO₃) and titanium tertbutoxide. The synthesized material characterized by scanning electron microscope, X-ray diffraction (XRD) and BET method. As can be seen from the SEM images, the B₂O₃/TiO₂ particles are very fine and the grain size is about 15–20nm levels. From these results, it can be concluded that nanoscale material could be obtained.

In order to characterize the nature of synthesized material, XRD pattern of the material was also investigated. According to the XRD pattern the nanoparticles are identified as crystalline B₂O₃ and ZrO₂. After showing the product was nano-scale B₂O₃/TiO₂, its specific surface area, which affects the adsorption characteristics of the material, was also investigated. The specific surface area of the prepared nano material was estimated to be 3.4m²/g by the BET method.

The pH values of model sample solutions prepared were adjusted to a range of 2–10 with HCl solutions keeping the other parameters constant and the general preconcentration procedure was applied. The optimum pH of the sample solution was 6 for effective adsorption of cadmium (II). At this pH value, the recovery of the cadmium (II) is above 95%. The decrease in the recoveries of the cadmium (II) at the lower pH values could be due to the competition between protons and the cadmium (II) for the adsorption sites of the sorbent. Therefore, a pH of 6 was selected in further experiments. The model cadmium solution (50 mL, 0.1 mg/L Cd (II)) was passed through the column with the flow rates adjusted in a range of 2–4 mL/min. The optimum flow rate was found as 2mL/min for Cd (II) ion. Therefore, a flow rate of 2mL/min was selected in further experiments. The flow rate of elution solution was 2 mL/min.

Fe-Mn Binary Oxide Adsorbent

Fe-Mn binary oxide originated by combining iron oxide and manganese dioxide has been prepared by several authors (Herranz *et al.* 2006; Zhang *et al.* 2007; Zhang *et al.* 2009). The Fe-Mn binary oxide adsorbent was synthesized from iron (II) sulfate heptahydrate (FeSO₄·7H₂O) and potassium permanganate solution (KMnO₄) under vigorous magnetic-stirring, and a 6 mol L⁻¹ NaOH solution was simultaneously added to keep the pH of the solution in the range of 7 and 8.

The specific surface area found by the BET method for Fe-Mn binary oxide was 201.8 m² g⁻¹, which indicates that the material has a high specific surface area, which is ideal for adsorption purposes. The total pore volume was 0.1738 cm³ g⁻¹ and the mean pore diameter was 3.4451 nm. The EDS results agreed well with the XRD results, indicating that the product obtained from the synthesis had Fe, Mn, and O as the major components. The SEM micrographs and EDS analysis of Fe-Mn binary oxide powders, shown that the particles had irregular surface morphology, and their particles sizes varied from 0.1 to 0.7 μm of length. The EDS analysis results confirmed that Fe-Mn binary oxide powders were chemically pure and were constituted principally of O, Fe, and Mn. The Fe-Mn binary oxide had a high affinity for Co (II) ions and that it was completely adsorbed from the solutions.

Regarding the adsorption capacities value obtained for the Co (II) adsorption on Fe–Mn binary oxide adsorbent with the prior data that has been collected in literature for Co (II) adsorption on Fe and Mn non binary oxides, The Fe–Mn binary oxide phase exhibit higher adsorption capacity toward heavy metals than the values obtained for other Fe and Mn oxide adsorbents such as: α -FeOOH, Fe₅O₇OH·4H₂O and Mn·MnO₂ (Backes et al. 1995),. Therefore, the results obtained indicated that the Fe–Mn binary oxide can be used in technologies aimed at water remediation to remove toxic metals as Co (II).

Table 4: Maximum adsorption capacities of Fe–Mn binary oxide (q_{max}) for Co (II) and other Fe and Mn oxide adsorbents

Adsorbents	Adsorption Capacities (q _{max} mg g ⁻¹)	References
Fe–Mn binary oxide	0.54	Granados, 2012
Fe -Oxide	10×10 ⁻²	Backes <i>et al.</i> , 1995
Mn-Oxide	18.82×10 ⁻²	Backes <i>et al.</i> , 1995
Fe(III)–Ti(IV) mixed oxide	85.0	Gupta <i>et al.</i> ,2009
Nano-TiO ₂	59.9	Pena <i>et al.</i> ,2009
Fe–Zr binary oxide	46.1	Gupta <i>et al.</i> ,2008
Zr-oxide	45.6	Zheng <i>et al.</i> .,2009
Fe-Cu binary oxide	82.7	Zhang, 2013
CuO nanoparticles	22.6	Martinson and Reddy, 2009
Nano Zro2/B2o3	32.2-109.9	(Özcan, <i>et al.</i> , 2011)

Fe–Zr Binary Oxide Adsorbent

The morphology of the Fe–Zr binary oxide was examined by a scanning electron microscope. The adsorbent particles are aggregated with many nanoparticles, leading to a rough surface and a porous structure. The particle size of this binary oxide is in the range 2–30 μ m. BET analysis shows that the sorbent has a specific surface area of 339m²/g with a pore volume of 0.21cm³/g. The sorbent presented a wide pore size range from 50 to below 1.5 nm.

Nanostructured iron (III)-copper (II) binary oxide

The Fe-Cu binary oxides were prepared from ferric chloride hexahydrate (FeCl₃·6H₂O) and copper (II) sulfate pentahydrate (CuSO₄·5H₂O). X-ray diffraction pattern of the oxide demonstrates two broad peaks this indicates that the prepared Fe-Cu binary oxide is amorphous. The SEM image of the oxide particles, showing that they are aggregates formed by small nanograins (around 50nm). The distribution of particle size of the powdered oxide is depicted indicating that main particle size of this binary oxide is in the range of 0.3-40 μ m. The amorphous Fe-Cu binary hydrous oxide has a high BET surface area of 282m²/g and a pore volume of 0.31cm³/g. The PSD pattern suggests that the pore is relatively uniform in size with an average pore size of 4.3 nm. The value of point of zero charge (PZC) of the Fe-Cu binary oxide is approximate 7.9). The PZC of pure ferrihydrite is about pH 7.4 (Zhang et al., 2012) and that of CuO is pH 9.4 (Yoon et al., 1979). Obviously, the incorporation of CuO with iron oxide makes the composite a higher PZC than that of pure ferrihydrite.

Ternary Mixed Oxide Nanocomposites

Wu *et al.*, 2007 studied and characterized sorption property of ternary mixed oxide nanocomposite. They examined the adsorption capacities, adsorption isotherm, and effect of pH, calcinations temperature, coexisting anions and kinetic effect of this adsorbent. The adsorbent showed a considerably high adsorption capacity over a relatively wide pH range and enhanced amount of surface active sites. For example, Fe-Al-Mn ternary mixed oxide nanocomposite and Fe-Al-Zr ternary mixed oxide nanocomposite are used to remove heavy metals from aqueous solutions.

Fe-Al-Mn Ternary Mixed Oxide Nanocomposites

Fe-Al-Mn ternary mixed oxide nanocomposite was synthesized by impregnating MnO₂ with Al and Fe nitrate aqueous solutions in deionized water. Nano sized Fe-Al-Mn ternary mixed oxides as a new solid phase extractor provides a simple, selective, accurate, economical, rapid and precise method for preconcentration and determination of heavy metals such as U (VI), Pb (II) and Cd (II) ions from aqueous solution. The maximum adsorption capacities of Fe–Al–Mn ternary mixed oxide nanosorbent for U (VI), Pb (II) and Cd (II) ions were found 14.9, 12.5 and 12.8 mg/g, respectively. It is noted that this value is higher as compared to the reported data (Nilofar and Ali, 2010).

Fe-Al-Zr Ternary Mixed Oxide Nanocomposites

The Fe-Al-Zr ternary mixed oxide nanocomposite was prepared by impregnation method (Aguila *et al.*, 2008). In which 0.1 molar nano sized Fe-Al-Zr ternary mixed oxide was prepared by impregnating ZrO₂ with Al and Fe nitrate aqueous solutions in deionized water. The surface morphology of the selected Fe – Al – Zr ternary mixed oxide nanocomposite was studied by scanning electron microscopy (SEM). The presence of Fe, Al and Zr elements in the mixed composite was determined based on the EDX results. The SEM image of Fe-Al-Zr nanocomposite indicated non uniform distribution of particles because of their irregular shapes. However apparently the proportions of the metals on this sample were found to be homogeneous.

Specific surface areas of the nanocomposites were determined using Brunauer–Emmett–Teller (BET) analytical methods. The specific surface area of the as-synthesized mixed oxide powder Was 56.81m²/g. The maximum adsorption capacities of Fe–Al–Zr ternary mixed oxide nanocomposite for heavy metals such as Cr (VI), Pb (II) and Cd (II) ions were found 20.53, 20.75 and 21.83 mg/g, respectively.

The pH point of zero charge of the adsorbent Fe-Al-Zr ternary mixed oxide nanocomposite was determined from the graph of final pH versus (final- initial) pH for 0.1 g of the adsorbent. The PH_{pzc} value is found to be 7.33. From this result, it can be concluded that basic modification of the adsorbent gave a negative (basic) surface charge for the adsorbent. The relationship between pH_{pzc} and adsorption capacity is that cations adsorption on any adsorbent will be expected to increase at pH value higher than the pH_{pzc} while anions adsorption will be favorable at pH values lower than the pH_{pzc} (Panumati *et al.*, 2008).

Factors Affecting the Adsorption of Heavy Metals

Various factors influence the adsorption capacity of potential adsorbents during the adsorption process. Previous researches have assumed that the efficiency of any adsorbent is strongly influenced by the physico chemical characteristics of the solutions such as pH, temperature, initial concentration, contact time and also adsorbent dose. A large portion of adsorption studies has been compiled to investigate the relationship of these parameters.

Effect of PH

Adsorption of heavy metal ions from the wastewater is mainly influenced by the pH of the solution. PH can influence the surface charge of the adsorbent, the degree of ionization also the species of adsorbate. At higher pH value, the adsorption of heavy metal ions showed a decrease due to precipitation of heavy metal ions forming bases on the surface of the nanocomposite. The precipitates block the pores of the nanocomposite which eventually led to the decrease in its adsorption capacity. On the other hand, at lower pH values, the H₃O⁺ ions compete with the metal ions for the exchange sites in the adsorbent and restricted the approach of the metal cations as a result of the repulsive force (bo-lin *et al.*, 2012). Based on these results, the best adsorption pH value for quantitative recovery of heavy metal ions was optimized pH value of the sample solution. Higher adsorption capacities can be obtained by optimizing the parameter (pH).

Effect of Temperature

Depending on the types of adsorbent used, temperature can affect the adsorption capacity of adsorbent. Temperature can change the adsorption equilibrium depending on the exothermic or endothermic nature of a process. The value of uptake capacity of adsorbents increases with the rise in temperature. The increasing sorption capacity of the sorbent with temperature is due to the enlargement of pores and/or the activation of the sorbent surface has been revealed (Han et al, 2006).

Effect of Initial Concentration

Initial concentration of metal ions can alter the metal removal efficiency through a combination of factors such as the availability of specific surface functional groups and the ability of surface functional groups to bind metal ions. Initial concentration of solution can provide an important driving force to overcome the mass transfer resistance of metal between the aqueous and solid phases (Malkoc and Nuhoglu, 2005). As the initial concentration of heavy metal ion increased, the adsorption removal had decreased which was probably due to the fact that at lower concentration, almost all heavy metal ions were adsorbed very quickly on the outer surface. However, further increase of the initial concentration of heavy metal ion leads to the fast saturation of adsorbent

3. CONCLUSION

The adsorption capacity is dependent on the type of the adsorbent used and the nature of the waste water treated. It is desirable to detect the heavy metal concentration in drinking water and also to provide a suitable, environment friendly and cost effective heavy metal removal process to save all over the world from heavy metal poisoning. So adsorption is a valuable tool for controlling the level of aqueous heavy metal pollution. The utilization of binary and ternary mixed oxide nanocomposite for the treatment of wastewater containing heavy metals is helpful as a simple, effective and economical means of wastewater treatment. Comparison between various adsorbents and its optimum conditions at maximum adsorption had been presented in the form of table for easy reference.

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