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Review article/Derleme makale

An Overview of Adsorption Technique for Heavy Metal Removal from Water/Wastewater: A Critical Review

Muharrem Ince[1*], Olcay Kaplan Ince[2]
[1]Munzur University, Faculty of Engineering, Department of Chemical Engineering, Tunceli, Turkey*
[2]Munzur University, Faculty of Engineering, Department of Food Engineering, Tunceli, Turkey
[*]E-mail: muharremince@munzur.edu.tr
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Abstract

Heavy metal pollution in the environment and effects on human health is within the most important issues. Because of continuous deterioration of water quality and persisting contamination level it has been observed and concerned by the scientists. Recently, to remove heavy metals from water/wastewater using various methods has been extensively studied. In conventional technologies, heavy metal removal/remediation is provided expensive because of non-regenerable materials used and high costs. Adsorption processes are being widely performed by several researchers for this purpose and various materials have been frequently used as adsorbent. It has been proved that adsorption is an effective method for purification, because of significant advantages including stability, utility, low-cost, ease of operation and performance. As adsorption technology is reduce the heavy metal ions concentrations to very low levels and because of using various low-cost adsorbent materials including biosorbents, clays, activated carbons, zeolites, metal oxides, it has major advantages. Metal adsorption onto adsorbent material, especially on agricultural wastes is a rather complex process because it is controlled by various factors. This process includes complexation, chemisorption, adsorption-complexation on surface and pores, micro precipitation, ion exchange. When used biological materials for adsorption process, some functional groups including sulphydryl, amido, hydroxyl and carboxyl, attach metal ions from water. This paper reviews the available adsorbent materials that have been used to heavy metal removal from water/wastewater and evaluates this technique advantages. Herein, the biosorbents such as banana peel, astragalus, chestnut sheel, natural adsorbents including clay also some artificial materials, like carbon-nanomaterials, zeolites, metal oxides, are reviewed as adsorbent materials for removal of different heavy metal ions like As(V), Pb(II), Cd(II), Cr(VI), Th(IV) and Eu(III) from water/wastewater.

Keywords: Adsorbent, adsorption processes, heavy metal, water/wastewater

Su/Atıksuda Ağır Metal Giderimi için Adsorption Tekniğine Genel Bir Bakış: Önemli Bir İnceleme

Öz

Çevredeki ağır metal kirliliği ve insan sağlığına etkileri en önemli konulardır. Su kalitesinin sürekli bozulması ve kirlenmenin devam etmesi nedeniyle, bilim adamları tarafından gözlemlenmekte ve endişe edilmektedir. Son zamanlarda, çeşitli yöntemler kullanarak ağır metallerin su/atık sudan uzaklaştırılması kapsamlı bir şekilde incelenmektedir. Geleneksel teknolojilerde, ağır metal uzaklaştırması/su kalitesinin iyileştirilmesi, kullanılan yenilenemez malzemeler ve yüksek maliyetler nedeniyle pahalıdır. Adsorpsiyon prosesleri bu amaçla birçok araştırmacı tarafından yaygın bir şekilde yürütülmektedir ve absorban olarak sıklıkla çeşitli malzemeler kullanılmaktadır. Kararlılık, yararlılık, düşük maliyet, kullanım kolaylığı ve performans gibi önemli avantajlardan dolayı adsorpsiyonun arıtma için etkili bir yöntem olduğu kanıtlanmıştır. Adsorpsiyon teknolojisi, ağır metal iyonu konsantrasyonlarını çok düşük seviyelere düşürdüğünden ve biyoadsorbanlar, killer, aktif karbonlar, zeolitler, metal oksitler gibi düşük maliyetli adsorban materyallerin kullanılması nedeniyle büyük avantajlara sahiptir. Adsorban materyali üzerine metalin adsorpsiyonu, özellikle de tarımsal atıklara metal adsorpsiyonu, çeşitli faktörler tarafından kontrol edilen oldukça karmaşık bir süreçtir. Bu işlem, kompleksleşme, kimyasal adsorpsiyon, yüzey ve gözeneklerde adsorpsiyon-kompleksleşme, ağır metal hidroksit yoğunlaşması, mikro çökelme, iyon değişimi içerir. Adsorpsiyon işlemi için biyolojik materyal kullanıldığında hidroksil, karboksil, sülfidril ve amido gibi bazı fonksiyonel gruplar sudaki metal iyonlarını tutarlar. Bu makale, sudan/atıksudan ağır metal gideriminde kullanılan adsorban materyalleri ve bu tekniğin avantajlarını değerlendirir. Burada, muz kabuğu, keven, kestane kabuğu gibi biyoadsorbanlar ve kilinde içinde bulunduğu

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doğal adsorbanlar, karbon nanomalzemeleri, zeolitler, metal oksitler gibi bazı yapay malzemelerin adsorban olarak As(V), Pb(II), Cd(II), Cr(VI), Th(IV) ve Eu(III) gibi farklı ağır metal iyonlarının sudan/atık sudan giderilmesi incelenmektedir.

Anahtar kelimeler: Adsorban, adsorpsiyon prosesi, ağır metal, su/atık su

INTRODUCTION

Heavy metals that have atomic density greater than 5 g cm^{-3} and atomic weights range from 63.5 to 200.6 such as arsenic (As), cadmium (Cd), chromium (Cr), lead (Pb), mercury (Hg) and nickel (Ni), are considered the major pollutants for fresh water reserves because of direct effect on living creatures (O'Connell et al., 2008; Srivastava and Majumder, 2008; Barakat, 2011; Fu and Wang, 2011). At the same time, they are non-biodegradable unlike organic contaminants and persistent in environment. When heavy metals release into ecosystem by various pollution source they have been causing worldwide problem. Particularly fast industrialization has caused releasing heavy metals into the environment and environmental pollution. The main sources of heavy metals are the wastewaters from modern industrial sources include chemical industries such as mining, metal plating facilities, surface coating, battery manufacturing, electrolysis, tannery, metallurgical, fossil fuel, paper and production of different plastics (Marques et al., 2009).

Even at trace level, exposure to heavy metals can cause risk for human beings (Jamil et al., 2010; Khan et al., 2008; Singh et al., 2010; Peng et al., 2004). Because of heavy metals tend to accumulate in living organisms and most of they are carcinogenic and teratogenic. They can cause various symptoms including organ damage, high blood pressure, reduced growth and development, speech disorders, sleep disabilities, fatigue, poor concentration, aggressive behavior, irritability depression, mood swings, increased allergic reactions, vascular occlusion, autoimmune diseases, oxidative stress and memory loss (Lee et al., 2012; Qu et al., 2013). Also they can disrupt the human cellular enzymes (Ageena, 2010).

Due to the increase in the importance of using friendly and economical new methods, studies on the production of adsorbents that can be used for this purpose have increased.

In many studies, several techniques such as adsorption, chemical precipitation, electrochemical technologies, ion exchange, membrane filtration and many other techniques are effective methods for heavy metal removal from contaminated water. (Wang et al., 2003; Kurniawan et al., 2006; O'Connell et al., 2008; Fu and Wang, 2011). However, from these mentioned techniques, adsorption is more advantageous in terms of economy, design and working flexibility, effectiveness, efficiency and high quality purified product. It is also important that the adsorbents used in the adsorption technique can be used repeatedly after some of the applied processes. (Pan et al., 2009; Zhao et al., 2011). Adsorption technique comes to the forefront, removal heavy metals from water/wastewater according to other techniques because of these advantages (Hua et al., 2012). So far, many researches have been investigations on sorption kinetics and thermodynamics, factors that affect sorption properties, possible absorption mechanisms and modification of adsorbents (Zhao et al., 2011).

In this article reviewed the suitability of adsorbents that used in adsorption technique for purification heavy metals from water/wastewater. In addition to the suitability of adsorbents, studies on the use of environmentally friendly, easily obtained and economical materials such as clay, astragalus, sawdust, and adsorbents obtained from the assessment of wastes such as chestnut shells, egg shells, tea waste and banana peel, are also considered in particular. The adsorption capacities of the adsorbents were also compared. Results revealed that these adsorbents have proved magnificent removal capabilities for most of heavy metal ions.

ADSORBENT TYPES

Activated Carbon

Because of large surface area and high number of pores, activated carbons have been used for heavy metals removal. This removal carries out by electrostatic attraction of metal ions to various surface oxygen-containing functional groups or by complexation reaction and it is easily prepared from readily available

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carbonaceous precursors such as coconut shells, chestnut shell and agricultural wastes. Because activated carbon is a low cost and its adsorption capacity is high it has been carried out various fields for purification including water. Because of having significant weak acidic ion exchange character, activated carbon is effective removing contaminants as trace metals and to adsorbing pollutants from wastewater. Chemical and physical treatments as functional surface modifications have been performed to increase the adsorption efficiency of activated carbon (Monser and Adhoum, 2002; Nadeem et al., 2006; Amuda et al., 2007; Yang et al., 2007; Afkhami et al., 2008). Especially surfactants that used for surface modification can increase significantly the activated carbons' heavy metal adsorption (Basar et al., 2003; Hong et al., 2008; Choi et al., 2009).

According to study of Ahn et al. (2009), to increase activated carbons capacity heavy metals adsorption, it was interacted with various chemicals such as sodium dodecyl benzene sulfonate, sodium dodecyl sulfate or dioctyl sulfosuccinate sodium. This study has also revealed that the realization of surface modification using anionic surfactant enhances the active carbon cation adsorb ability.

Anirudhan and Sreekumari (2011) derived activated carbon from waste coconut buttons. Industrial effluents were purified from Pb(II), Hg(II) and Cu(II) ions by using batch adsorption techniques and the results indicated that the produced activated carbon was proper to remove for these metals. Their characterization were made by elemental analysis, fourier transform infrared (FTIR), X-ray diffraction (XRD), scanning electron microscope (SEM), thermogravimetric analysis (TGA), differential thermal analysis (DTA), surface area analyzer and potentiometric titrations. They optimized parameters that are effective on study as adsorbent amount, stirring time, initial metal concentration and pH. Activated carbon exhibited a very good adsorption potential for studied heavy metals.

In a similar study, a Tunisian olive-waste cake was used preparation of activated carbon for Cu(II) removal. Phosphoric acid was used for chemical activation of activated carbon. In order to improve the chemical characteristics of the adsorbent surface it was treated with potassium permanganate and after this processes their Cu uptake capacity was enhanced (Baccar et al., 2009).

Demiral and Güngör (2016), used grape bagasse to obtain activated carbon. They applied phosphoric acid for chemical activation and after this procedure activated carbon was carried out to purification of aqueous solutions from Cu(II). SEM, Boehm titration and FTIR spectroscopy techniques were used to characterize the adsorbent. They found that the highest 1455 m^2 g^{-1} of surface area and 0.88 cm^3 g^{-1} of total pore volume obtained at a carbonization temperature of 500 ºC with an impregnation ratio of 5/1.

Şahin and Saka (2013), using acorn shell for obtaining activated carbons by physical activation with H_2O–CO_2 in two-step pretreatment including $ZnCl_2$-HCl at 850 °C. They characterized it by N_2 adsorption, FTIR, SEM and Brunauer-Emmett-Teller (BET) surface area analysis. Adsorption capacity of activated carbons were demonstrated by the iodine numbers. The maximum surface area of activated carbon was found to be around 1779 m^2 g^{-1}.

Demirbas et al. (2009), obtained activated carbons using hazelnut shell and activated carbons were used Cu(II) ions removal from aqueous media in a batch adsorption system. Activated carbons adsorption capacity was obtained as 58.27 mg g^{-1} for Cu(II). Optimum experimental conditions were reported as adsorbent amount (0.5-3.0 g L^{-1}), initial metal concentration (25-200 mg L^{-1}), temperature (293-323 K) and pH (2-6).

Biosorbents

Because of to be new process using low-cost adsorbents derived from agricultural materials, biosorption is preferred by a lot of researchers to perform in various studies especially to remove heavy metals from aqueous effluents. Biosorption have some advantages including eco-friendly, inexpensive, high efficiency, reuse and possibility of metal recovery compared with adsorption other techniques. Commonly, the uses of food waste or agricultural residues are preferred because they contain three major structural components including hemicelluloses, cellulose and lignin.

Qi and Aldrich, (2008) investigated tobacco dust that a typical lignocellulosic agricultural residue for heavy metal adsorption efficiency.

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They reported that it set out a strong capacity for heavy metals including Cd(II), Zn(II), Ni(II), Pb(II) and Cu(II), and because their adsorption amount on biosorbent was calculated as 29.6 mg g^{-1}, 25.1 mg g^{-1}, 24.5 mg g^{-1} 39.6 mg g^{-1}, and 36.0 mg g^{-1}, respectively. *Solanum melongena* leaves were used as inexpensive biosorbent material by Yuvaraja et al. (2014). They characterized and used it to remove Pb(II) from aqueous solutions. Experimental data revealed that the biosorption processes of Pb(II) compatible with pseudo-second-order kinetics and maximum sorption capacity of biosorbent was found 71.42 mg g^{-1} for Pb(II) ions.

Witek-Krowiak et al. (2011), studied Cr(III) and Cu(II) ions biosorption from aqueous media using peanut shell under different experimental conditions for example biomass amount, temperature and pH. Based on biosorption equilibrium isotherms of peanut shells, their adsorption capacity was calculated for Cr(III) and Cu(II) as 27.86 mg g^{-1} and 25.39 mg g^{-1} Cu(II), respectively. Some biomass materials including *Eichhornia crassipes*, were used as dried biomass for heavy metals (Cr, Cd, Pb, Ni, Cu, and Zn) removal from aqueous media (Verma et al., 2008). Results revealed that all the biomass were efficiently removed Zn, Cd and Pb from aqueous media. Ni(II), Cu(II), Pb(II) and Zn(II) sorption on a waste product of the paper industry were investigated by Guo et al. (2008). They reported that lignin had affinity with metal ions from aqueous solution following order: Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II). To remove Cu(II) from aqueous solutions several biomass shells such as rice and wheat were performed by Aydın et al. (2008). They found the maximum adsorption capacities as 8.977, 9.510 and 9.588; 7.391, 16.077 and 17.422; 1.854, 2.314 and 2.954 mg g^{-1} for lentil, wheat and rice adsorbents for Cu(II) at 293, 313, 333 K, respectively. Ince et al. (2017), investigated Cu(II) ion adsorption onto various dried biomass such as banana peel, chestnut shell, and tea leaf waste in aqueous solutions. Several experimental parameters that influence on adsorption such as contact time, adsorbent amount and pH were performed. Developed method using these food waste biomass adsorbents were applied to mineral water and industrial wastewater samples and their Cu(II) removal potentials were compared. Based on results, maximum adsorption capacity of banana peel, chestnut shell, and tea waste were found as 1.94 mg g^{-1}, 2.25 mg g^{-1}, and 3.36 mg g^{-1}, respectively. Ince and Kaplan Ince (2017) using Box-Behnken design approach for removal of copper from wastewater performed several experimental parameters that influence on adsorption. Ince, (2014) used tea waste, astragalus plant and chestnut shell as inexpensive and environmentally friendly biosorbents for Ni(II) removal from aqueous solutions. Their adsorption capacity for Ni(II) was found to be 5.4 mg g^{-1}, 1.3 mg g^{-1} and 5.6 mg g^{-1}, respectively.

This study pointed out the utilization of ecofriendly and low-cost biosorbents as an alternative natural adsorbent for Ni(II) ions removal. In another study, Ince and Kaplan Ince (2017) were to apply the Box–Behnken experimental design and response surface methodology for modeling of Cu(II) ions from an industrial wastewater and leachate pretreated astragalus herbal plant. Three independent variables (pH, contact time, and adsorbent amount) were studied. The significance of the independent variables and their interactions were tested by means of the analysis of variance (ANOVA). Biomass adsorption capacity was found as 1.98 mg g^{-1}. Brinza et al. (2007), studied heavy metals removal from wastewater using various algal biomasses. Also it was reported that the ability of algal species to remove heavy metals from wastewater depends on process or environmental factors. When compared uptake capacities of algal biomass for heavy metal removal it was found brown algae uptake capacities higher than red and green algae.

Carbon Nanotubes

With the development of technology, interest in the production and use of carbon nanotubes with unique morphology has increased. Surface sorption properties were developed to remove heavy metals from liquid solutions. Gupta et al. (2011), produced multiwall carbon nanotubes (MWCNTs) as a magnetic adsorbent. It was characterized by XRD, field emission scanning electron microscope (FESEM) and FTIR. The carbon nanotubes adsorption capability was compared with activated carbon both batch and fixed bed modes. It was observed that MWCNTs adsorption capability superior to activated carbon. According to results, as carbon nanotubes have high surface area and this feature

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provides the advantage that they can be used as an adsorbent for the treatment of contaminated water. Kabbashi et al. (2009) investigated Pb ions removal from aqueous media by carbon nanotubes (CNTs) using a batch experimental mode. They obtained maximum Pb(II) removal as 83-85% under effective parameters for experiment including CNTs dosage, contact time, agitation speed, and pH. A MWCNTs was modified with 8-hydroxyquinoline by Kosa et al. (2012) and carried out to remove of Cu(II), Cd(II), Zn(II) and Pb(II) under optimum experimental conditions (MWCNTs; 250 mg, pH; 7.0 K; 298 K). Li et al. (2010), used CNTs as adsorbents in wastewater treatment and their adsorption capacity was calculated as 67.9 mg g^{-1} for copper. Gao et al. (2009) prepared oxidized CNTs to investigate metal ions sorption and factors affecting sorption mechanisms. Li et al. (2015), prepared a new CNTs composite using various reaction and their structure including physical and chemical properties characterized by FTIR spectroscopy, TGA and SEM. It is adsorption performance was evaluated for Zn(II), Cd(II) and Cu(II) and adsorption mechanism were discussed. CNTs exhibited a good adsorption potential for Cd(II), Cu(II) and Zn(II) and obtained maximum adsorption capacities as 11.2 mg g^{-1}, 167.2 mg g^{-1} and 98.1 mg g^{-1} respectively. Pyrzynska and Bystrzejewski (2010), compared some adsorbents sorption potential for Cu(II) and Co(II) adsorption amount. According to results, CNTs and carbon-encapsulated magnetic nanoparticles have significantly higher adsorption efficiency for these metal ions. It was mentioned in a similar study, using various kinds of CNTs were used to remove some ions including Ni(II), Cu(II), Cd(II), and Pb(II) from aqueous solution. Also CNTs are promising because they can be used environmental protection application especially for metal ions removal because of the superior sorption capacity and effective desorption (Rao et al., 2007). Because of good adsorption potential for heavy metals and they can apply for environmental protection CNTs have been used on a wide scale by a lot of researchers.

Clays

Because of some characteristic properties including high cation exchange capacity, large surface area, chemical and mechanical stability and layered structure, clays have high sorption capacity for heavy metals. Because of these advantages, a large number of researchers were used clay to adsorb several pollutants especially heavy metal ions from aqueous media (Rozic et al., 2000). Montmorillonite acts as a potential ionic exchanger for heavy metals because of its easy manipulation, high abundance, eco-friendly and harmlessness to the environment among natural clays (Chen et al., 2003; Bhattacharyya and Gupta, 2006; Orhan and Kocaoba, 2007; Abou-El-Sherbini and Hassanien, 2010; Vieira et al., 2010; Wu et al., 2011; Turan and Ozgonenel, 2013). Abou-El-Sherbini and Hassanien (2010) used Na-montmorillonite clay as adsorbent to remove Cu(II). They characterized modified clay using TGA, FTIR and XRD. In experiment, some parameters that effected adsorption were investigated. Study results revealed that modified clay shows good removal efficiency for Cu(II) ions. The removal capacity was determined as 119 mEq 100 g^{-1} at pH 3.0–8.0 and with 10 min stirring time. Modified clay was carried out different samples to remove Cu(II). Clays like kaolinite, montmorillonite, and their poly(oxo zirconium) and tetrabutylammonium derivatives utilized as adsorbent material for purification Cu(II) from aqueous solutions. These clays were confirmed using XRD and results revealed that kaolinite, montmorillonite and derivatives could be used as adsorbent for separation of Cu(II) from these solutions (Bhattacharyya and Gupta, 2006). Orhan and Kocaoba (2007) were studied some heavy metals removal, including Cr and Pb from aqueous solutions using natural and modified zeolites. To improve the zeolites' heavy metal adsorption capacity, samples were modified by HNO_3 or NaOH. Removal efficiencies and kinetics were determined for heavy metals. They studied effects of heavy metal initial concentration on the removal percentage and described Freundlich and Langmuir isotherm constants and correlation coefficients. Abollino et al. (2003) used Na-montmorillonite as adsorbent for adsorption some metal ions and this adsorbent adsorption was better for Cd, Cr, Cu, Mn, Ni, Pb and Zn metal than other investigated metal ions. Al-Degs et al. (2006) investigated natural Jordanian clay adsorption performance for Co(II), Pb(II) and Zn(II) ions removal from aqueous solutions and they determined it was an effective adsorbent.

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Vieira et al., (2010) characterized clay using XRD, BET and energy dispersion X-ray (EDX) analysis and they examined the influence of parameters including temperature, pH and adsorbent dosage. To identify potential adsorption process mechanisms, kinetic models were evaluated. The Langmuir model provided the best fit for sorption isotherms and the bofe clay removed Ni with maximum adsorption capacity (1.91 mg g^{-1} (metal/clay)) under optimum conditions. Wu et al., (2011) reported that montmorillonite is a potential economical adsorbent for various kinds of heavy metals ions including Cd(II), Cu(II) and Cr(III) from aqueous solutions. Modified montmorillonite by humic acid was characterized by powder XRD and FTIR spectroscopy. They mentioned that results showed that the modified clay adsorption capacity for these metal ions were higher than raw clay. Both Langmuir and Freundlich model were used for equilibrium data. Based on results, Langmuir model provided better correlation than the Freundlich model. Ince (2014) studied to detect clay adsorption performance for Ni(II) from aqueous medium under optimum batch experimental conditions. FTIR spectroscopies of clay samples before and after Ni loaded were investigated and by using these spectra functional groups that took Ni were determined. Adsorption capacity of clay was stated 19.4 mg g^{-1} for Ni(II).

In addition, several researchers reported that treatment of clay with a chemical such as hydrochloric acid caused an increasing surface area of the raw clay. This increase was up to fivefold. Depending on surface area increasing, heavy metal removal capacity of the clay was increased, too (Christidis et al., 1997; Unuabonah et al., 2008).

Metal Oxides

Nanosized metal oxides such as ɣ-Fe_2O_3, TiO_2, MnO_2 and ɣ-Al_2O_3 are environmentally benign and demonstrate amphoteric sorption behaviors because of specific affinity and high surface area for heavy metal adsorption from aqueous media. New technologies has been recently developed to synthesize effective metal oxides. Various modern analytical techniques including FTIR and nuclear magnetic resonance (NMR) were used to reveal the underlying mechanism responsible for metal removal. A lot of researchers investigated and intended to develop metal oxides' heavy metals removal performance under experimental conditions. They can act like Lewis acids-bases and capable of binding transition metal for example Cd(II), Zn(II), Ni(II), Cu(II), and Pb(II). Also they demonstrate high specific sorption capacity at nanoscale owing to sorption sites reside predominantly on the surface (Sarkar et al., 2011; Hua et al., 2012). MnO_2 (Caliskan et al., 2011), ZnO (Chen et al., 2015) , ɣ-Fe_2O_3 (Hu et al., 2008), TiO_2, ɣ-AlOOH, and ɣ -Al_2O_3 etc. (Zhao et al., 2011) were used metal-oxides as adsorbents and they were applied to various matrix. Under different temperatures, natural diatomite and MnO_2-modified diatomite adsorbents was performed by Caliskan et al. (2011), for Zn(II) removal from aqueous media. They reported that Zn(II) ions adsorption onto diatomite based on a physical mechanism. Karami (2013), investigated Pb, Fe, Cu, Ni, Zn and Cd removal from aqueous solutions using a new effective adsorbent that was synthesized by electrochemical method and their name is magnetite nanorods. New adsorbent was characterized by SEM and XRD. Langmuir isotherms results demonstrated that nano-magnetite adsorbent capacity were found for Cu(II), Cd(II), Ni(II), Zn(II), Pb(II) and Fe(II) as 79.10, 88.39, 95.42, 107.27, 112.86 and 127.01mg g^{-1}, respectively. Pan et al., (2010), developed a Fe_2O_3 hybrid adsorbent and they reported that it was set out effective adsorption performance for Pb(II) and Cd(II) from natural waters. In a similar study, iron oxide was used for metal ions such as Pb(II), Ni(II), Cd(II) and Cu(II) from solutions using batch method by Phuengprasop et al. (2011). Fe-oxide coated sludge maximum adsorption capacity was found for metals range from 7.8 mg g^{-1} to 42.4 mg g^{-1}. Furthermore, they reported that Fe-oxide coated sludges' can be used for metal removal from wastewater. Manju et al. (2002), synthesized iron(III) oxide as adsorbent and used for Cd(II), Pb(II) and Hg(II) removal, it sets out a very high adsorption potential for these heavy metals. Diatomite and manganese oxide were tested by Majeda et al. (2004), for Cd(II), Pb(II) and Cu(II) removal from wastewater. Experimental studies showed that diatomite has a higher removal capacity for these metals from water than untreated diatomite. They reported that as Mn-oxides quantity deposited on the Mn-diatomite surface their adsorption capacity was increased. Similarly, TiO_2 was applied as adsorbent for Ni(II) ions removal from natural and industrial wastewater by Debnath et al., (2009). They investigated TiO_2 synthesis and characterization besides Ni(II) adsorption behavior and also pointed out that the Fe(III) ions showed a strong negative influence on Ni(II) sorption to TiO_2. In heterogeneous aquatic systems, TiO_2, γ -AlOOH and γ -Al_2O_3 hydrous oxides were investigate for Fe(II) adsorption to iron-free mineral surfaces (Nano and Strathmann, 2006).

Zeolites

Zeolites are acted as ion-exchange materials because of structural characteristics and valuable properties. Therefore, zeolites are widely used for metal ions removal from the aqueous medium because of their easily ion exchange with the metal cations, relatively high specific surface areas, high ion-exchange capacity besides low prices. Most of zeolites are the most abundant and they have high selectivity for certain pollutants such as heavy metals (Zhao et al., 2011). Bosco et al., (2005) investigated Brazilian natural zeolite cation-exchange capacity for Cd(II), Ni(II), Cr(III), and Mn(II) in synthetic aqueous effluents and developed method was applied wastewater. According to Freundlich isotherm, the results revealed that Brazilian natural zeolite have a good removal performance for metals removal. Chunfeng et al. (2009), synthesized pure-form Cu and Zn gel zeolites and their adsorption capacity compared with a commercial zeolite to remove heavy metal from aqueous media. Some natural zeolites including mordenite, clinoptilolite and modified zeolites were performed to remove As(V) from aqueous media. Results revealed that modified zeolites were more effective adsorbent for As(V) removal from aqueous solutions (Chutia et al., 2009). To recover Eu(III), Fe(III) and Th(IV) from aqueous medium Sharma et al. (2009) synthesized and characterized an analogue of heulandite zeolites. According to results, synthetic analogue of heulandite showed maximum adsorption capacity for Eu(III) and Fe(III).

CONCLUSION, RECOMMENDATIONS AND PROSPECTS

As a result of industrial activities, various pollutants including Pb, Cd, Cu and Cr are released into environment and contaminate water. Industrial establishments are obliged to treat the heavy metal content specified by law to reduce their concentration to acceptable levels. Great numbers of researcher have been used various techniques for removing pollutants especially heavy metals from water/wastewater because of limited water resources and increasing pollution levels. As adsorption technique is versatile and it removes diverse pollutants. Therefore, among these techniques adsorption technique is widely preferred. The present study suggests that various types of adsorbents including natural materials such as biosorbents, clay minerals and some of materials modified to improve their adsorption capacity including carbon-materials, metal oxides are summarized. The metal ions adsorption amounts onto various adsorbents and under different experimental conditions besides relationship between adsorption properties and capacity was discussed. When considering the adsorbents economy, recyclable, effective and low-cost, adsorbents should be synthesized for its extensive application in our daily life. In the future, if adsorbent materials have high sorption ability and surface area, easily separation from aqueous solution, enough functional groups and environmental friendship they may preferred for heavy metal removal. Adsorption process and materials that is cheap, practical and efficient should be explored further for the possibility of heavy metals recovery from water/wastewater. However, obtained big progress there is still a need for continued development of inexpensive and effective adsorbents because of their performance. In addition, when alternative adsorbents that highly efficient for heavy metal removal and eco-friendly are preferred may contribute to both sustainable an environment and protects human health. Undoubtedly, these materials offer many promising benefits for a clean and livable future.

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