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REVIEW ARTICLE

Removing Heavy Metals from Industrial Wastewater: Review Advanced Methods

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ABSTRACT
One of the most important issues in today's world is environmental pollution to hazardous and toxic metals. Heavy metals are in wastewater of many industries such as the zinc extraction industries, petrochemical, etc. So, the industrial wastewater before joining the municipal wastewater refinery system needs the treatment and removal of heavy metals. It is clear that the implementation of recovery techniques and investment in this area will create the possibility of compensation as a part of expenditure for wastewater treatment, while saving in the consumption of these metals by industries. The present study deals with the existing methods and their effectiveness in the removal and recovery of heavy metals from wastewater industry. Common methods of removing heavy metals from wastewater can be chemical precipitation, chemical oxidation and revival, surface adsorption, electro dialysis, filtration and membrane processes such as reverse osmosis and nano-filtration. Physicochemical methods mentioned above are expensive and need to invest a lot for the construction and exploitation. In addition, bioaccumulation has a low capability to compete with conventional technologies to remove heavy metals from the water environment. Therefore, for effective removal of heavy metals from water and wastewater, there is an urgent need to develop a new, low-cost and economic method.
Keywords: *wastewater treatment, physic-chemical methods, heavy metal, reduction*

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INTRODUCTION
One of the most important issues in today's world is environmental pollution to hazardous and toxic metals. Extraction of metals from the mines and extensive use of heavy metals in the industry has led the concentration of these metals be increased in water, wastewater, air and soil higher than background values [1]. The mechanism of the toxic effects of heavy metals caused by the intense desire of the metal cations to sulfur and thereby disrupting the activity of vital enzymes in living organisms [2]. Therefore, the removal of heavy metals from aquatic environments is an important issue in public health that is important in two respects:
A) Separation of heavy metals from industrial wastewater, agricultural drainage, mines and neutralizes their toxic effects
B) The recycling of metals that is necessary with the gradual decline of harvesting the mineral resources
Heavy metals are in wastewater of many industries such as the zinc extraction industries, petrochemical, oil refining industries, paper industries, pharmaceutical industry, paint industry, plastic products industry, etc. In the case of progressing to wastewater treatment systems, they influence the microorganisms and synthetic reactions of wastewater treatment due to their toxicity characteristics and led to the reduced efficiency of system [3, 4].
This causes the concentration of these compounds in the sewage existing from the mentioned refinery does not match with the standards set by national and international authorities. On the other hand, entering of the heavy elements and compounds to environment have irreversible impacts on the environment and human being. According to the above mentioned issues, the purification of these compounds and their removal is very important in accordance with domestic and international standards

[5]. The existence of heavy metals in urban sewage in the refinery system has caused the disruption and reduced the purification efficiency and in extreme cases, stopped biological activities of refinery systems [6].
So, the industrial wastewater before joining the municipal wastewater refinery system needs the treatment and removal of heavy metals. It is clear that the implementation of recovery techniques and investment in this area will create the possibility of compensation as a part of expenditure for wastewater treatment, while saving in the consumption of these metals by industries. The present study deals with the existing methods and their effectiveness in the removal and recovery of heavy metals from wastewater industry [7, 8].

CONTEXT

Heavy metals such as copper and zinc eventually expose human being to side effects of toxicity, carcinogenic, short-term and long-term genetic effects due to features such as accumulation in tissues, inseparability, resistance to biological interactions and toxicity by achieving to the food chain and living organisms [9]. Therefore, treatment and removal of metals from waste water before discharging into the environment is essential. Different physico-chemical and biological methods can be used to remove heavy metals [10].

Ion exchange method

Ion exchangers are insoluble and solid materials with anions or cations that are exchangeable when ion exchangers interact with an electrolyte solution. These ions can be exchanged with existing ions in solution with the same charge as an equivalent amount of stoichiometry [11].
In ion exchange, the cations and anions present in the solution are replaced with existing cations and anions in the resin in a way that both solution and resin remain electrically neutral. It should be noted that a solid-fluid balance is raised. In other words, without solving the solid in a solution, some dissolved ions and resin are exchanged with each other [12]. Ion exchange resins are divided into two groups of cationic and anionic resins. Each group consists of strong and weak one. In general, strong resins carry out ion exchange in a wide range of pH and weak resins do it in a very small range of pH [13].
Cation resins must be kept in the 40-120 F^0 and anion resins of chloride form are maintained in 40-120 F and hydroxide form in 40-95 F^0. Freezing and melting of the resin leads to the breaking and cracking them [13, 14]. In reduction process of resin, the ions that are absorbed from wastewater will be replaced with ions of reduction material and resin returns back to the initial state (15). Advantages of this method include: This process is very selective and can be accompanied with the elimination of special substrate. Design and operational experience is accessible. The units can be operated manually or automatically [2,15].
The high cost of disposing during the recovery stage, low life expectancy of resin in the face of high pollution, high costs of revival, etc. are among its limitation [16]. In the following, we discussed the details of how to recover heavy metals used by ion exchange method.

Nickel

Nickel recovery can be accomplished by using the ion exchange process. Recovery usually requires separating the wastewater flow, especially if there is a cyanide ion. The presence of this substance causing the permanent contamination of resins [17, 18]. Nickel usually exists in the form of Sulfate, therefore; sulfuric acid is applied for the process of resins' recovery. But if nickel recycles from wastewater of nickel refining units, the refining material of resin will be ammonium carbonate [19].

Copper

Ion exchange method, the copper removal is done properly when the sewage is diluted. The removal of copper is reported from the concentrations of 1.02 to less than 0.03 milligrams per liter. But generally, ion exchange method is appropriate for the recovery of copper from wastewater having copper at least 200 milligrams per liter [17-19].
One of the important applications of ion exchange in the recovery of copper is wastewater purification related to the process, copper ammonium, in rayon industry (rayon). In this system, using a weak acid cation exchanger, copper ions, as well as ammonia and water is recycled and re-used in the process [19].

Waste water's Containing Complex Materials

A kind of sewage which is not purified with conventional ion exchangers are wastewaters which heavy metal ions existing in them that are attached to an organic molecule and form a complex molecule. Ammonia is one of the possible combinations. Copper complexes are removed by the fork shape resins [18].

In the primary sewage, the complex has a positive charge. Therefore, it will be removed by means of a cation exchanger. But in the high pH, the complex has no charge, so it will be restored using an alkaline resin [17].

Zinc

Ion exchange method not only is a recovery method, but also it is a complete purification method (Polishing) to achieve the desired standard of output. It can also be applied for water recovery and reusing [17]. Many of cationic resins act selectively than conventional bivalent ions such as calcium and magnesium. But about the zinc cations, the lack of such selective function leads to faster saturation of resin [20]. In general, the purification of wastewater containing zinc with ion-exchange method merely does not have much economic value [18].

Mercury

Recovery and reuse of mercury from industrial wastewater decrease approximately 25% of the purification cost. Resins that have a strong tendency to mercury ions, holds on of one of the following groups:

- (-SH) named thiol with hydrochloric acid as a reduction
- (-NH-C-HS) named ISO thiouronium with thiourea as reduction in hydrochloric acid solution
- (HS C-NH) named Sithiocarbamate with sodium sulfide as a reduction materials

Also, the strong alkaline resins can be used. Mercury is absorbed in the form of complex $HgCl_4^{-2}$. (20)

Gold and Silver

In the case of wastewater containing precious metals such as gold and silver, efforts have been on the full recovery of these metals. In wastewater containing gold, this metal exists in the form of anionic cyano complexes Au $(CN)_{-2}$. The strong alkaline resin has the ability to absorb this complex [21].

$RN^+RX^- + Au\ (CN) \rightarrow RN^+R_3\ Au(CN)_2^- + X^-$

This process does not need to adjust the pH, unless the environment is extremely alkaline. If the strong alkaline resin is used, it is necessary to adjust the pH between 7 and 9.

The most important topic of silver recovery is in the photographic industry. This wastewater containing complex Ag $(S_2O_3)^{3-}$. The strong alkaline resin is normally used for recovery of silver from resin in the reduction stage is carried out using ammonium chloride. Silver in this solution, will be deposited after contacting with iron pellets [22].

Chromium

Ion exchange process for the removal and recovery of chromium has been reported as an economical method. Cation exchanger is used to remove the trivalent chromium and anionic exchanger in order to remove chromate and dichromate. When saturated, the anion exchanger is restored with alkaline, which is usually used by sodium hydroxide. The result of output solution is sodium chromate. The generated sodium chromate passes from the cation resin and Utah chromic acid recycles with a concentration of about 6 percent. One of the examples of using ion exchangers in the recovery of chromium is recycling of chromate $(CrO)_4^{-2}$ existing in wastewater of cooling towers and returning it to the system [18, 22].

The Process of Electric Coagulation and Clotting

Today, the coagulation and clotting process in water and wastewater purification is commonly done through the addition of chemical & organic coagulants, minerals and so on to the environment of water and sewage [23]. The methods of chemical composition haven't significant benefits due to limitations such as high costs of operation and adverse environmental consequences unlike the relatively long history of using in the water and wastewater industry. Therefore; in order to find other appropriate strategies to replace the process of chemical composition, various methods have been studied in recent years among them are the process of electrical coagulation and flotation as a considerable innovation in the water and wastewater industry [24].

Electric coagulation is the production of coagulants in place by using electrical breakdown of aluminum or iron electrodes. The production of metal ions is carried out in the anode and hydrogen gas at cathode. In this technique, the colloidal particles existing in the environment of water or wastewater which act as anode and cathode using electrodes and installed electrical current from aluminum, iron, etc. neutralize through the production of electrical positive charges and as a result, it provides Al^{+3}& Fe^{3+} , and so on in the clotting process [16, 25].

Effective Factors in Electric Flotation

Size and dimension of bubbles generated in the electric flotation is largely depended on the pH value. At neutral pH, tiny bubbles of hydrogen are formed. In electrical flotation, with increased pH, the diameter of oxygen bubbles increase in that anode [26]. The diameter of the bubbles produced in this process depends on the electrical current entering to the electrodes and by increasing this parameter, the diameter of produced bubbles increases. It is noteworthy that the amount of applicable current should be taken based on existing relationships or pilot studies. The location and position of anode and cathode electrodes significantly influence on the amount of gas production [27].

The Application of Electric Coagulation Process in Treatment of Wastewater

This method can be useful for purifying of industrial, urban and agricultural wastewater. Among the industries which this method had a very successful results are metal industries & factories (automotive, lathing, car bodies, etc.), industries of extracting heavy metals from mines, (plating industries) and etc. [28].

The process of coagulation and electric flotation process by taking advantages such as lower volume of generated sludge, lower operating costs, more favorable environmental and health aspects and higher efficiency than the process of chemical precipitation in removing pollutants from water and sewage has a very favorable prospect in water and wastewater industry [27].

The current disadvantages of this method is the high cost of investment of this system which the related investment costs will be reduced to a large extent in case to provide the required condition to make and create a part of discussed equipment inside the country. A significant reduction in the concentration of chemical contaminants, synthetic and toxic including heavy metals that have a deterrent effect on the biological activity of microorganisms, This system has been widely used in many industrial and agricultural wastewater and in practice, the application of biological purification processes in terms of such pollutants are facing with many constraints. This is why, the appropriate approach for the removal of these pollutants is very important [29].

The process of electric coagulation is not cost effective for small purifying systems. We can reduce the costs by means of aluminum ingots in this way. With appropriate utilization, we can apply this method for a long period of time [28].

PACT Process

The combined process of active carbon powder- activated sludge (PACT) apply as a process for purifying industrial wastewater with high organic load and the presence of Irresolvable or deterrent compositions of microbial growth such as heavy metals.

In the last three decades, the application of PACT process has been widely used for purification in the industrial wastewater [30].

Application of this method due to achieve similar efficiencies with other advanced methods and investment costs, and lower operation as well as simplicity in the equipped operating systems and relatively simple operation, control and operation of units has been welcomed in recent decades in many industrial centers and urban and industrial wastewater treatment plants specially for purifying of industrial wastewater and fast removal of degradable organic load, Late degradable organic materials, special organic and mineral compounds such as paints, metals, polycyclic compounds and deterrents of growth [31].

Studies and experiences show that the most important reason to increase the efficiency of removing the heavy metals in such systems are the increased absorption and fast growth of bacteria and improvement of deposited properties of produced clotting [30].

In this process, wastewater injected by pumping from the sewage reservoir to the aeration unit and provides the required air by compressor. And for uniform distributing of air bubbles and creating uniform mixing conditions in aeration units of air diffusers will be embedded in parallel on the floor of aeration unit. Returning sludge by an airlift pump enter in the entrance side and mixed liquid exit from the adjustable overflow output. A mixture of active carbon powder and water formed in the cylindrical tank and inject by a dosing pump into the aeration unit. Mixing act of carbon powder and water is done by secondary air valve (lateral branch of the windpipe) within the required time [31].

Ectrochemical methods for the analysis of organic & inorganic contaminants (e.g heavy metals) and industrial wastewater

Electrochemical methods described in this section (Figure 1) for analysis of organic and inorganic substances in wastewater can be divided into two main parts. Direct electrolysis processes include the methods of cathode reduction and anodic oxidation. And indirect electrolysis process includes the following methods:

- Mediated oxidation and reduction: like the factors which are produced and reversible as electrolyte.
- Strong anodic oxidation: like irreversible electrolytic factors O_3, ClO_2, Cl_2, ClO^-
- Strong cathode oxidant Like H_2O_2
- Common methods of dividing phase such as electrocoagulation, and electro-flotation and electro-flocculation [32].

Electrolysis is a process unit which chemical changes resulted from the electron transport through the common interface between the solution and the electrodes. Electric current is supplied by a direct electric current and advance applied voltage between two electrodes in a reaction cell. Electric current is supplied by a direct electric current and voltage applied between two electrodes in a cell's response to earlier. The figure 1 shows a profile of an electrochemical reactor for the removal of heavy metals (33).

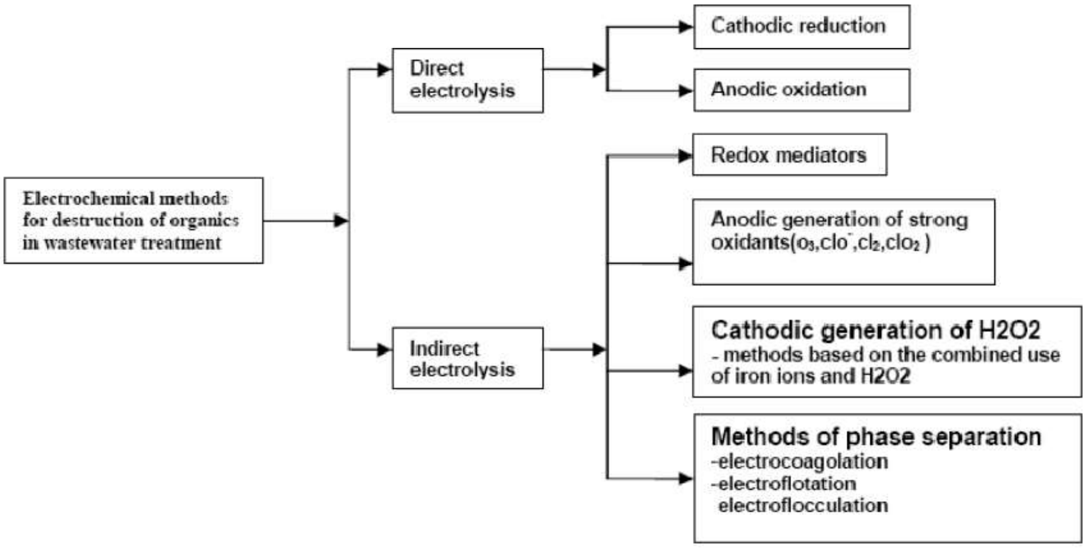

Figure 1. The classification of electrochemical methods for the decomposition of organic materials in wastewater [33]

Nanotechnology

Nanotechnology involves imaging, measurement, using of producing objects between the scales of 1 and 100 nanometers. The benefits of Nanotechnology are the manufacturing of new products, durability and longer life and low energy consumption. The nanotechnology has wide applications in the environment. Nanoparticles are of great flexibility in filtering pollutants. In case of using conventional methods to purify organic solvents containing chlorinated compounds such as trichloroethylene and vinyl chloride that are created by lateral and harmful reactions. Using nano- bimetallic particles (two metals with nano dimensions) bring the production of such undesirable side products to zero. Hardware-based nano-structured particles are capable of degrading stable pollution compounds such as nitrates, heavy metals (nickel and mercury) and radioactive materials such as uranium dioxide. Nano-particles are used for the immediate treatment of sediment, water purification and liquid wastes [15, 34].

Nano filtration is the separation of materials from the solvent by passing the solution through a membrane with a pore diameter in the range of 0.5 to 2 nm. Driving factor in this process is applying differential pressure in the range of 5 to 40 times. Pore diameter is so that molecules are separated from the solution with a molecular weight of 300 to 500 grams per mole. Surface membrane has a slight electrical charge and thus the electrical interaction between different ions as well as the surface membrane plays a major role in the isolation of these elements from the solution [35].

Wastewater treatment by means of nonophotocatalyst can simultaneously remove organic and inorganic compounds and convert wastewater to a suitable water supply. As these compounds are bio-degradable, we are forced to use some kind of energy to break them. This energy comes from sunlight and it is used with light catalysts. The generated electricity from the cell reaction of catalysts can break degradable compounds. This process is very cost-effective due to recycling from the light catalyst. The additional effect of different metals is known in improving catalytic activity and it is applied by scientists in removing trichloroethylene (TCE) from underground waters. The researches of Environmental Nanotechnology Center (CBEN), in the University of the Rhine indicate that gold and palarym nanoparticles are very effective catalyst for removing the pollution TCE from water. Using nanotechnology can increase the number of atoms in contact with TCE molecules as well as the efficiency of the catalyst several times than popular catalyst [36].

Researchers at Rice University have developed a new technique which produces titanium Nano-crystals with high surface area to remove organic aromatics. These materials find the capability of optical oxidation of many molecules under the ultraviolet radiation. Further, the C_{60} is a very good optical catalyst which its performance is hundreds of times more than available Titanium in the market (34).

Bioabsorption Method

Bioabsorption is physic-chemical uptake of heavy metals by microorganisms (bacteria, fungi, algae) and other organic objects (such as rice bran, peel of fruit, leaves and bark of trees, etc.). Benefits of bioabsorption process compared to conventional methods for removal of heavy metals including cost-effectiveness, the property of selective adsorption, the possibility of bioadsorbents reduction and recycling of metals, high speed of process and the lack of sludge production. Using physical and chemical pretreatment can improve the performance of bioadsorbents. The studies show in the area of bioadsorbents that some bio adsorbents have a high adsorption capacity for heavy metals. The introduction of these organic materials to industry leads to the production of some commercial products which is used for removing heavy metals from wastewater in full scale [37].

However, the most important factor compared to bioadsorbents with each other and other methods of removing heavy metals is the absorption capacity for desired metal, but since the experimental conditions (temperature, pH, initial concentration of metal, ratio of adsorb to the adsorbent and so on) affect the absorption capacity, we should also consider this condition for comparison, which makes it difficult to compare the results of different studies [38].

In recent years, the researches about bioadsorbents are focused on organic waste objects (such as fermentation process and active sludge produced in urban wastewater treatment plants) and abundant organic matter in the environment (such as seaweed) [39].

The proven active mechanisms involved in the process of bioabsorption are surface absorption, ion exchange, chelating, microprecipitation, oxidation and revival reactions. According to the type of bioadsorbents, several mechanisms act simultaneously to remove metals in bioabsorption process [40].

Among the commercial bioabsorbents AMT-BIOCLAIM™, AlgaSorb™ and Bio-Fix. AlgaSorb™ are produced by using algae *Chlorella vulgaris* and used for wastewater treatment. This product is applied for the removal of metal ions in the initial concentration 1-100 mg/L. Output concentration is less than 1 mg/L, the calcium and magnesium ions has no impact on its performance and does not reduce its absorption capacity [41].

DISCUSSION AND CONCLUSION

Common methods of removing heavy metals from wastewater can be chemical precipitation with lime and soda, ion exchange processes, chemical oxidation and reduction, surface adsorption, electro dialysis, filtration and membrane processes such as reverse osmosis and nanofiltration. Physicochemical methods mentioned above are expensive and need to invest a lot for the construction and exploitation and in many cases with the help of these methods; there is no access to legal standards wastewater discharge. It should be noted that the above-mentioned technologies are used in areas with high concentrations of heavy metals and if the concentration of heavy metals is low in sewage, these technologies do not have necessary effectiveness and will be costly [11-14].

The most common method of removing heavy metals from wastewater is chemical deposit. In this method, in order to achieve discharge standards, a huge amount of chemicals should be used. Thereby, a voluminous sludge is produced which increases treatment costs. The other popular methods of removing heavy metals from wastewater can be the process of ion exchange, surface adsorption, membrane and oxidation processes which are expensive and have high investment costs and operation [17-19].

The removal of heavy metals have been observed in the conventional systems of municipal wastewater treatment, but higher concentrations of heavy metals in accepted capacity have adverse effects on biological processes of wastewater treatment, so the conventional systems of biological wastewater treatment are not suitable for detoxification of wastes containing high concentrations of heavy metals [25-27].

Visiting the ability of existing microorganisms in biological systems of wastewater treatment for the removal of heavy metals has been the founder of further studies in this area. Bioaccumulation is an active and dependent removal to metabolism of heavy metals in resistant & accumulated microorganisms. Active uptake of heavy metals is critical by microorganisms in environmental conditions (temperature, pH, etc.)[42].Bioaccumulation requires nutrients to survive microorganisms, in addition; the capacity of active adsorption of heavy metals by microorganisms is relatively small, thus Bioaccumulation has a low capability to compete with conventional technologies to remove heavy metals from the water environment. Therefore, for effective removal of heavy metals from water and wastewater, there is an urgent need to develop a new, low-cost and economic method. Some studies have been developed in the field of bioabsorption in recent years to meet this need [34-36].

REFERENCES

1. Gupta ,V.K., Gupta, M., & Sharma, S., (2001). Process development for the removal of lead and chromium from aqueous solution using red mud – an aluminum industry waste. Water Res., 35 (5):1125–1134.
2. Kadirvelu, K., Thamaraiselvi, & Namasivayam, K., C., (2001). Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Bioresour. Technol., 76 (2001):63–65.
3. Chand, S., Aggarwal, V.K., & Kumar, P., (1994). Removal of hexavalent chromium from the wastewater by adsorption. Indian J. Environ. Health, 36 (3):151–158.
4. Mohan, D., Singh, K.P., (2002). Single and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse – an agricultural waste. Water Res., 36 (2002):2304–2318.
5. Khan, N.A., Ali, S.I., & Ayub, S., (2001). Effect of pH on the removal of chromium (Cr) (VI) by sugar cane baggase. Sci. Technol., 6 (2001):13–19.
6. Ayub, S., Ali, S.I., Khan, N.A., Rao, R.A.K., (1998) Treatment of wastewater by agricultural waste. Environ. Prot. Control J., 2 (1) (1998):5–8.
7. Ayub, S., Ali, S.I., Khan, N.A., (2001). Study on the removal of Cr(VI) by sugarcane bagasse from wastewater. Pollut. Res. J., 2 (2):233–237.
8. Ayub, S., Ali, S.I., Khan, N.A., (2002). Adsorption studies on the low cost adsorbent for the removal of Cr(VI) from electroplating wastewater. Environ. Pollut. Control J., 5 (6):10–20.
9. Srinivasan, K., Balasubramaniam, N., Ramakrishna, T.V., (1998). Studies on chromium removal by rice husk carbon. Indian J. Environ. Health, 30 (4):376–387.
10. Munaf, E., Zein, R., (1970). The use of rice husk for removal of toxic metals from wastewater. Environ. Technol., 18 (1970):359–362.
11. Ajmal, M., Rao, R.A.K., Anwar, S., Ahmad, J., Ahmad, R., (2003). Adsorption studies on rice husk: removal and recovery of Cd (II) from wastewater. Bioresour. Technol., 86 (2003):147–149.
12. Suemitsu, R., Venishi, R., Akashi, I., Nakano, M., (1986). The use of dyestuff-treated rice hulls for removal of heavy metals from waste water. J. Appl. Polym. Sci., 31 (1986):75–83.
13. Khan, N.A., Shaaban, M.G., Jamil, Z., (2003). Chromium removal from wastewater through adsorption process, in: Proc. UM Research Seminar 2003 organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur.
14. Ajmal, M., Rao, R.A.K., Siddiqui, B.A., (1996). Studies on removal and recovery of Cr (VI) from electroplating wastes. Water Res., 30 (6):1478–1482.
15. Kadirvelu, K., Kavipriya, M., Karthika, C., Radhika, M., Vennilamani, N., Pattabhi, S., (2003). Utilization of various agricultural wastes for activated carbon preparation and application for the removal of dyes and metal ions from aqueous solution. Bioresour. Technol., 87 (2003):129–132.
16. Selvi, K., Pattabhi, S., Kadirvelu, K., (2001). Removal of Cr (VI) from aqueous solution by adsorption onto activated carbon. Bioresour. Technol., 80 (2001):87–89.
17. Tan, W.T., Ooi, S.T., Lee, C.K., (1993). Removal of chromium (VI) from solution by coconut husk and palm pressed fibre. Environ. Technol., 14 (1993):277–282.
18. Khan, N.A., Shaaban, M.G., Hassan, MH.A., (2003). Removal of heavy metal using an inexpensive adsorbent, in: Proc. UM Research Seminar organized by Institute of Research Management and Consultancy (IPPP), University of Malaya, Kuala Lumpur.
19. Ayub, S., Ali, S.I., Khan, N.A., (2001). Efficiency evaluation of neem (Azadirachta indica) bark in treatment of industrial wastewater. Environ. Pollut. Control J., 4 (4):34–38.
20. Bailey, S.E., Olin, T.J., Bricka, Adrian, R.M., D.D., (1999). A review of pontentially low-cost sorbents for heavy metals. Water Res., 33 (11):2469–2479
21. Wong, K.K., Lee, C.K., Low, K.S., Haron, M.J., (2003). Removal of Cu and Pb by tartaric acid modified rice husk from aqueous solution. Chemosphere, 50 (2003):23–28.
22. Abu Qdaisa, H., Moussab, H., (2004). Removal of heavy metals from wastewater by membrane processes: a comparative study. Desalination, 164 (2004):105–110.
23. Abu-Eishah, S.I., (2008). Removal of Zn, Cd, and Pb ions from water by Sarooj clay. Appl. Clay Sci., 42 (1–2):201–205.
24. Ahluwalia, S.S., Goyal, D., (2006). Microbial and plant derived biomass for removal of heavy metals from wastewater. Bioresour. Technol., 98 (12):2243–2257.
25. Ahmady-Asbchin, S., Andre‘s, Y., Ge´rente, C., Le Cloirec, P., (2008). Biosorption of Cu(II) from aqueous solution by Fucus serratus: surface characterization and sorption mechanisms. Bioresour. Technol., 99 (2008):6150–6155.
26. Alinnor, J., (2007). Adsorption of heavy metal ions from aqueous solution by fly ash. Fuel, 86 (2007):853–857.
27. Amana, T., Kazi, A.A., Sabri, M.U., Bano, Q., (2008). Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. Colloids Surf. B: Biointerfaces, 63 (2008):16–121.
28. Trivunac, K., Stevanovic, S., (2006). Removal of heavy metal ions from water by complexation-assisted ultrafiltration. Chemosphere, 64 (3):486–491.
29. Wang, L., Wang, N., Zhu, L., Yu, H., Tang, H., (2008). Photocatalytic reduction of Cr(VI) over different TiO_2 photocatalysts and the effects of dissolved organic species. J. Hazard. Mater., 152 (2008):93–99.

30. Yoona, J., Shimb, E., Baec, S., Jooa, H., (2009). Application of immobilized nanotubular TiO_2 electrode for photocatalytic hydrogen evolution: reduction of hexavalent chromium (Cr(VI)) in water. J. Hazard. Mater., 161 (2–3):1069–1074.
31. Mubarak, N. M., (2014). Removal of heavy metals from wastewater using carbon nanotubes. Separation & Purification Reviews, 43(4): 311-338.
32. Chatterjee, S. K., I. Bhattacharjee, and G. Chandra., (2010). Biosorption of heavy metals from industrial waste water by Geobacillus thermodenitrificans. J. Hazard. Mater., 175(1): 117-125.
33. Mohammadi, T., Mohebb, A., Sadrzadeh, M., Razmi, A., (2005). Modeling of metal ion removal from wastewater by electrodialysis. Sep. Purif. Technol., (41):73–82.
34. Nah, I.W., Hwang, K.Y., Jeon, C., Choi, H.B., (2006). Removal of Pb ion from water by magnetically modified zeolite. Miner. Eng., 19(14):1452–1455.
35. Wang, L.K., Vaccari, D.A., Li, Y., Shammas, N.K., (2004). Chemical precipitation. In: Wang, L.K., Hung, Y.T., Shammas,N.K. (Eds.), Physicochemical Treatment Processes, vol. 3. Humana Press, New Jersey, pp. 141–198.
36. Wang, L., Wang, N., Zhu, L., Yu, H., Tang, H., (2008). Photocatalytic reduction of Cr(VI) over different TiO2 photocatalysts and the effects of dissolved organic species. J. Hazard. Mater., (152): 93–99.
37. Zhang, F.S., Itoh, H., (2006). Photocatalytic oxidation and removal of arsenite from water using slag–iron oxide–TiO2 adsorbent. Chemosphere, 65 (1): 125–131.
38. Zuoa, W., Zhanga, G., Mengb, Q., Zhangb, H., (2008). Characteristics and application of multiple membrane process in plating wastewater reutilization. Desalination, (222):187–196.
39. Igwe, J.C., Ogunewe, D.N., Abia, A.A., (2005). Competitive adsorption of Zn(II), Cd(II) and Pb(II) ions from aqueous and non-aqueous solution by maize cob and husk. Afr. J. Biotechnol., 4 (10): 1113–1116.
40. Jakobsen, M.R., Rasmussen, J.F., Nielsen, S., Ottosen, L.M., (2004). Electrodialytic removal of cadmium from wastewater sludge. J. Hazard. Mater., 106(B):127–132.
41. Juang, R.S., Shiau, R.C., (2000). Metal removal from aqueous solutions using chitosan-enhanced membrane filtration. J. Membr. Sci., (165):159–167.
42. Kajitvichyanukula, P., Ananpattarachaia, J., Pongpom, S., (2005). Solgel preparation and properties study of TiO2 thin film for photocatalytic reduction of chromium(VI) in photocatalysis process.Sci. Technol. Adv. Mater., (6):352–358.