Sorbents for Contaminants Uptake from Aqueous Solutions. Part I: Heavy Metals

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Abstract: Heavy metal pollution is an environmental problem of worldwide concern. Several industrial wastewater streams may contain heavy metals such as; Pb, Cr, Cd, Ni, Zn, As, Hg, Cu, Ag. A wide range of low-cost adsorbents has been studied worldwide for heavy metal removal. It is evident from our literature survey that in expensive and locally available materials could be used instead of conventional expensive adsorbents. Natural adsorbents as peat moss, fiber sludge ash, fly ash, pine bark, sawdust, shrimp coal reject, olive stone, straw, automobile tyres, seaweed, sewage sludge, bagass, fertilizer waste, ores, raks, plant straw and dried aquatic plants are one of the effective and environmentally sound low coast material for treatment of polluted water from heavy metals. The equilibrium sorption capacities of Pb ions were determined and found to be respectively 4.38 and 3.77 mg/g for activated carbon (AC) and seed hull at 60°C. It has been well known that chitosan demonstrates the unique adsorption ability towards many metal cations as compared to AC. The preliminary results indicate that treated olive stone (TOS) exhibit a better efficiency in terms of sorption capacities toward cadmium (128.2mg/g) than reported so far in the literature. It was reported that the adsorption capacity of lignin for Pb and Zn ions was found to be 1.865 and 95 mg/g respectively at 40°C. The removal of Pb (II), Cd (II) and Zn (II) from aqueous solution by indigenous clay was decreased from 80.3% to 51.3% by increasing the temperature from 30 to 50°C. The maximum heavy metal ion adsorbed by tourmaline was found to be 78.86, 154.08, 67.25 and 66.67 mg/g for Cu, Pb, Zn and Cd respectively. The abundant, natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents.

Key words: Heavy metals • Conventional sorbents • Low-cost sorbents • Sorption kinetics • Wastewater

INTRODUCTION

Environmental pollution, as a consequence of industrialization process, is one of the major problems that has to be solved and controlled [1]. Land disposal of municipal and industrial wastes and application of fertilizers and pesticides in agriculture has contributed to continuous accumulation of heavy metals in soil and there is increased concern regarding the environmental impacts of agriculture practices of the bioavailability of heavy metals [2]. The bioavailability and mobility of these metals in soil strongly depends on the extent of their sorption with solid phases. Heavy metals are not degradable and have increasing significant owing to their harmful effect on human physiology and other biological systems when they exceed the tolerance levels and become an ecotoxicological hazards of prime interest. They pose a significant threat to the environment and public health because of toxicity, incremental accumulation in the food chain and persistence in the ecosystem [3,4]. The toxic metal must be effectively treated /removed from the wastewaters. If the wastewaters were discharged directly into natural waters, it will constitute a great risk for the aquatic ecosystem, whilst the direct discharge in to the sewerage system may affect negatively the subsequent biological wastewater treatment [5]. The commonly used procedures for removing metal ions from aqueous streams include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction. Adsorption is an effectively purification and separation technique used in water and wastewater treatments [6]. Increase in variety and amount of hazardous chemicals in effluents makes conventional adsorbents inefficient and sometime even ineffective. Consequently, the development of new and more effective adsorbents has become essential, at the same time it should be of low cost. Thus research interest into the production of cheaper adsorbent (like biosorbents) to replace costly

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wastewater treatment technologies [7]. Biosorption, based on metal binding capacities of various biological materials. Biosorption can be defined as the ability of biological materials to accumulate heavy metals from wastewater through metabolically mediated or a physico-chemical pathway of uptake. The major advantages of biosorption over conventional treatment methods are: low cost, high efficiency minimization of chemical and biological sludge no additional nutrient requirement regeneration of biosorbent and possibility of metal recovery.

Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay or certain waste product from industrial operations such as fly ash, coal and oxides are classified as low-cost adsorbents.

The purpose of this paper is to review the available information on various attributes of utilization of natural, agricultural, microbial and many other types of sorbents to explore the possibility of exploiting them for heavy metal removal from contaminated water.

Technologies for Removal of Heavy Metals: A number of technologies for the removal of heavy metal ions from aqueous solution have been developed over the years [6]. The most important of these technologies include: chemical precipitation, filtration, ion-exchange, electrolysis, lime coagulation, solvent extraction, reverse osmosis and electrocoagulation [8]. Electrocoagulation is an efficient method where the flocculating agent is generated by electro-oxidation of a sacrificial anode, generally made of iron or aluminum. In this process, treatment is done without adding any chemical coagulant or flocculants, thus reducing the amount of sludge, which must be disposed. A great deal of work performed in the last decades has proved that electrocoagulation is an effective technology for the treatment of heavy metal containing solutions. However, all these technologies have their inherent advantages and limitations in application [9, 10]. Most of these methods suffer from some drawbacks such as incomplete metal removal, low selectivity, high reagent and energy requirement, high capital and operational cost and generation of toxic sludge or other waste product that require careful disposal has made it imperative for a cost effective treatment method. Adsorption technology is generally considered to be promising method amongst the different existing technologies[11], because of its high efficiency and complete removal of metal ions at low concentration, easy separation of sorbent from aqueous media after treatment, cheap easy to adopt and has been proven to be successful method for removal of heavy metals from wastewater [12]. Numerous empirical models for single solute systems have been employed to describe the sorption equilibrium [13], namely Langmuir, Freundlich, Brunauer-Emmett-Teller (BET), Sips, Dubinin-Radushkevich, Temkin and Toth models. Langmuir and Freundlich equations are the most popular and widely used models in a large number of studies. Pseudo-first and second-order rate expressions have been and still in wide-use for studying the biosorption of heavy metals from aqueous solutions. In chemisorption process, the pseudo-second order is superior to pseudo-first order model as it takes into account the interaction of adsorbent-adsorbate through their valence forces. Majority of the studies on sorption of heavy metal ions by diverse kinds of sorbents have focused on the single metal uptake. In contrast to this ideal condition, various types of metals present in wastewater [13]. Another discouraging fact, the equilibrium modeling of multi-metal sorption, which is essential in the design of treatment systems, was often neglected. In the practice, examination of the effects of binary metal ions in various combinations is deemed to be more representative than the single-metal studies. One of the major concerns arising from the adsorption of heavy metals from wastewater is the simultaneous presence of miscellaneous metals in wastewater. The interference and competition between different metals, metals and solvents as well as metals and adsorption site are significant enough to be taken into account, leading to a more complex mathematical formulation of the equilibrium.

Conventional Sorbents for Heavy Metals: Major conventional adsorbent are, activated alumina, silica gel, activated carbon, molecular sieve carbon, molecular sieve zeolites [14].

Activated Carbon: Activated carbon has been frequently used as an adsorbent for the removal of heavy metals from aqueous solution[14,15].

Since its first introduction for heavy metal removal, AC undoubtedly been the most popular and widely used adsorbent in waste water treatment application, throughout the world. In spite of its prolific use, AC remains an expensive material since higher the quality of AC, the greater its cost. AC also requires complexing agents to improve its removal performance for inorganic matters. Yadav et al. [16] used granular activated carbon(GAC) and powder activated carbon (PAC) as adsorbent to remove the trace metal arsenic from aqueous solution. Their results show that adsorption capacity of GAC was much more than that of AC.
Despite its extensive use in the water and wastewater treatment industries, AC remains an expensive material. Three types of AC; C₁, the waste generated from sugar industry as waste product and the others (C₂ and C₃) were commercial GAC, were used for removal and recovery of chromium [17]. The adsorption process and the extent of adsorption were dependent on the physical and chemical characteristic of the adsorbents, adsorbate and experimental condition.

The efficiencies of the removal and the order of selectivity of Cr (III) were found to be C₁ > C₂ > C₃. The performance of 17 carbon based adsorbents, were compared for the removal of dissolved copper from water [18]. Twelve of the adsorbents studied were peat of different types, geographic origin and processing history. The remaining adsorbents were lignite, lignite char, bone char and two ACs. The capacity of each adsorbent was determined from batch tests and the results showed a wide range of performance. The most effective adsorbent was bone char with capacity of approximately, 100 mg Cu per gram of bone char.

Chen et al [19] prepared AC from sewage sludge to produce a useful adsorbent for pollutant removal as well as for dispose of sewage sludge. The kinetic and thermodynamic of adsorption of Pb onto AC from coconut (CAC) and seed hull (GA) of the palm trees were studied [20]. The equilibrium sorption capacities of Pb ions were determined and found to be respectively 4.38 and 3.77 mg/g for AC and seed hull at 60 °C. The values of thermodynamic parameters show that the adsorption is endothermic and non spontaneous. A comparative study on the removal of Cr (VI) from aqueous solution was carried out using low-cost adsorbents derived from used tyers (TAC), sawdust (SPC) and granular activated carbon (GAC) [21]. It was found (Table 1) that the adsorption capacity of SPC is significantly lower than that of both TAC and GAC. It can be explained due to the fact that both TAC and GAC have similar particle size (0.2 mm) lower than SPC (0.65 mm). It was also indicated that the adsorption of Cr(VI) was more favorable at higher temperature.

Soil: The capacity of soil to retain and release metals can be an important factor to product environmental impact of the use of residues such as sewage sludge containing heavy metal [22]. Adsorption and desorption of heavy metal have been correlated with soil characteristics such as, pH, redox potential, clay minerals and soil organic matter. Sorption desorption and immobilization of Pb, Cd and Zn by an artificial soil produced open air composting of sewage sludge of Vienna, wood shaving green composed and sandy loam were studied. Artificial soil had a greater capacity for adsorption of Pb, Cd and Zn.

Contaminated soil often presents an unacceptable risk to human and ecological health and must be remediated [23], chemical immobilization is an in situ remediation method where inexpensive materials such as fertilizer and waste products are added to contaminated soil to reduce the solubility and bioavailability of heavy metals. The effect of application of sewage sludge (SW) and compost (C) to the soil (S) on the Cu and Cd sorption, distribution and the quality of the dissolved organic mater (DOM) in the soil was investigated under controlled condition [24]. The results showed application of either sewage sludge or compost increased the Cu sorption capacity of soil. While the sewage sludge and compost application did not increase the Cd availability in the soil.

Non-Conventional Low-Cost Sorbents for Removal of Heavy Metals
Agricultural Sorbents: In recent years, the need for safe and economical methods for the elimination of heavy metal from contaminated waters has recesitated research interest towards the production of low cost alternatives to commercially available activated carbon. Therefore there is an urgent need that all possible sources of argo-based inexpensive adsorbent should be explored and their feasibility for the removal of heavy metal should be studied in detail [14]. Less expensive adsorbents and their utilization possibilities for various agricultural wastes by products are; sugar can bagass, rice husk, olive palm shell, coconut shell husk for elimination of heavy metal from wastewater. Agricultural material contains protein, polysaccharides and lignin which are associated with functional groups responsible for metal ion adsorption. The abundant natural occurrence and presence of large amount of surface functional groups make various agricultural wastes good alternatives to expensive synthetic adsorbents [25]. Tamarind fruit shell (TFS) was used as an adsorbent for Cu (II) from aqueous solution in the presence of N, N'-methylenebisacrylamide as a cross-linking agent [26]. The detailed analysis of the R² values (Table 2) showed that the Langmuir model fit the adsorption data better than the Freundlich model at different temperatures, which indicates that Cu (II) ions adsorbed on TFS-CB as a monolayer adsorption. It is clear from Table 2, that adsorption capacity increases with the increase in temperature, thereby indicating the process to be endothermic in nature. The kinetics of adsorption of Cu (II) followed pseudo-second order model and the rate constant increased with increase in temperature. The maximum adsorption capacity for Cu (II) was found to be 64.10 mg/g.
Table 1: Comparison of the adsorption capacities of low-cost adsorbents (TAC and SPC) and GAC at different temperatures (21)

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Types of adsorbents</th>
<th>Adsorption capacity (mg/g)</th>
<th>$\Delta G^\circ$ (KJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>TAC</td>
<td>48.08</td>
<td>-12.33</td>
</tr>
<tr>
<td></td>
<td>SPC</td>
<td>1.93</td>
<td>-1.17</td>
</tr>
<tr>
<td></td>
<td>GAC</td>
<td>44.44</td>
<td>-2.37</td>
</tr>
<tr>
<td>303</td>
<td>TAC</td>
<td>55.2</td>
<td>-12.92</td>
</tr>
<tr>
<td></td>
<td>SPC</td>
<td>2.16</td>
<td>-3.30</td>
</tr>
<tr>
<td></td>
<td>GAC</td>
<td>48.54</td>
<td>-4.35</td>
</tr>
<tr>
<td>311</td>
<td>TAC</td>
<td>58.48</td>
<td>-13.86</td>
</tr>
<tr>
<td></td>
<td>SPC</td>
<td>2.29</td>
<td>-5.06</td>
</tr>
<tr>
<td></td>
<td>GAC</td>
<td>53.19</td>
<td>-6.94</td>
</tr>
</tbody>
</table>

Table 2: Adsorption isotherm constants for Cu (II) adsorption on TFS-CE (26)

<table>
<thead>
<tr>
<th>Isotherm Models</th>
<th>Cu (II)/TFS-CE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
</tr>
<tr>
<td>Langmuir Qm (mg/g)</td>
<td>64.100</td>
</tr>
<tr>
<td>b (dm^3/mg)</td>
<td>0.360</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich Kf</td>
<td>21.260</td>
</tr>
<tr>
<td>n</td>
<td>4.040</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.854</td>
</tr>
<tr>
<td></td>
<td>313 K</td>
</tr>
<tr>
<td>Langmuir Qm (mg/g)</td>
<td>79.920</td>
</tr>
<tr>
<td>b (dm^3/mg)</td>
<td>0.520</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich Kf</td>
<td>25.820</td>
</tr>
<tr>
<td>n</td>
<td>4.180</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.833</td>
</tr>
<tr>
<td></td>
<td>323 K</td>
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<tr>
<td>Langmuir Qm (mg/g)</td>
<td>76.330</td>
</tr>
<tr>
<td>b (dm^3/mg)</td>
<td>0.970</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich Kf</td>
<td>32.320</td>
</tr>
<tr>
<td>n</td>
<td>4.580</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.807</td>
</tr>
<tr>
<td></td>
<td>333 K</td>
</tr>
<tr>
<td>Langmuir Qm (mg/g)</td>
<td>81.330</td>
</tr>
<tr>
<td>b (dm^3/mg)</td>
<td>1.760</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.999</td>
</tr>
<tr>
<td>Freundlich Kf</td>
<td>40.590</td>
</tr>
<tr>
<td>n</td>
<td>5.240</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.754</td>
</tr>
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</table>

Olive Stones: Olive stones are an agricultural waste predominantly produced in Mediterranean countries [27]. The material resulting from their carbonization has been successfully used as sorbents for a wide variety pollutant in aqueous solution. The preliminary results indicate that treated olive stone (TOS) exhibit a better efficiency in terms of sorption capacities toward cadmium (128.2 mg/g) than reported so far in the literature. Moreover the sorption process is ascertained to occur fast enough so that equilibrium is reached in less than 15 min of contact time. Areas planted with olive trees in the Mediterranean region are increasing due to the continual demand for olives as nutrients [28]. Solid residue of olive mill products (SROOMP) was employed potentially to treat drinking water containing several heavy metals in trace concentration, namely Cr (111), Ni (11), Pb (11), Cd (11) and Zn (11), different experimental approaches including equilibrium batch model experiments, scanning electron microscope (SEM) and X-ray fluorescence (XRF) were used to explore the feasibility of this material as an adsorbent for the removal of these heavy metals from aqueous solution. Results indicate that SROOMP can be used to remove Pb (11) and Zn (11) but not other metals investigated in their study.

Ashes: A study was carried out by Zhang et al. [29], to prepare low-cost adsorbents from different types of wastes and ashes. The BET surface area of the adsorbents ranged from 115 to 485 m2/g. Heavy metal leaching from these adsorbents was greatly reduced compared to leaching from the bulk ashes. The adsorption of heavy metal on the prepared adsorbents was not in accordance with their surface area because acidic sites reaction, adsorption affinity and cation exchange all contribute to the adsorption on adsorbents.

Peach and Apricot: A study was conducted to determine the suitable conditions for the use of peach and apricot stones, produced from food industries as a solid waste, as adsorbent for the removal of lead ion from aqueous solution containing this ion [30]. Natural adsorbents as ores, raks, peach, apricot, plant straw and dried aquatic plants are one of the effective and environmentally sound low coast material for treatment of polluted water from heavy metals. The results revealed that adsorption of Pb (11) on peach stone was stronger than on to apricot stones up to 4% at 5 hrs adsorption time. Suitable equilibrium time for the adsorption was 3-5 hrs, 95% Pb adsorbed on apricot and 97% on peach. The effective adsorption PH was in the range 7-8. Application of
Table 3: Metals uptake by lignin at different temperatures (34)

<table>
<thead>
<tr>
<th>Type of Metal</th>
<th>Temperature (K)</th>
<th>( \Delta G^o ) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>305</td>
<td>313</td>
</tr>
<tr>
<td>Lead</td>
<td>1586</td>
<td>1865</td>
</tr>
<tr>
<td>Zinc</td>
<td>73.24</td>
<td>94.83</td>
</tr>
</tbody>
</table>

Langmuir and Freundlich isotherm models show high adsorption maxima and high binding energy using these adsorbents for the removal of Pb ions from contaminated water and wastewater.

**Sewage Sludge:** Adsorption of Cd, Cu, Pb and Zn from aqueous solution by sewage sludge, paper mill waste (PMW) and composted paper mill waste was investigated [31]. Sewage sludge was the most effective biosorbent of the waste products for all metals examined, adsorbing, for example up to 39.3 mg/g of Pb at an initial concentration of 77.8 mg/L. However, it was found that composting paper mill waste resulted in an increased in metal uptake capacity and both sewage sludge and composted paper mill waste have potential for low cost remediation of high leachate wastewaters.

An aerobically digested sludge [32], was used as an adsorbent for Cd (11), Cu (11), Ni (11) and Zn (11) from aqueous solution. Based on the maximum adsorption capacity obtained from the Langmuir and the Redlich-Peterson isotherm the affinity of the studied metals for the sludge has been established as Cu (11) > Cd (11) > Zn (11) > Ni (11). Adsorption from multielement system revealed that the adsorption capacity for Cu (II) is not reduced by the presence of the other above referred metals.

**Industrial By-Products:** The removal of heavy metals, Cr (VI), Cd (II) and Al (III) from wastewater using adsorbents such as waste tea, Turkish coffee, exhausted coffee, nut and walnut shells was investigated [33]. Batch studies showed that these adsorbents exhibit a good adsorption potential for Al (III). The adsorption ratio of Al (III) were as 98, 99, 96, 99.5 and 96% for waste tea, Turkish coffee, exhausted coffee, nut and walnut shells, respectively from wastewater.

Adsorption of Lead and Zinc ions onto lignin extracted from black liquor was carried out [34]. Black liquour, a waste product originated from paper industry. It was reported (Table 3) that the adsorption capacity of lignin for both ions was found to be 1865 and 94.83 mg/g respectively at 40°C. Results indicated that the high adsorption capacity of lignin is due to the presence of polyhydric phenol groups on the surface of lignin. It was also indicated that the adsorption is an endothermic process, since a higher removal was favored at higher temperature.

**Biosorbents:** Biosorption is the ability of biological material to accumulate heavy metals from wastewater through metabolically mediated or physico-chemical pathways of uptake. Algae, bacteria and fungi and yeasts have approved to be potential metal biosorbents [35].

**Chitosan:** Several adsorbents, such as active carbon, herbaceous peat, fiber, rice husk, sawdust and starch have been used for removing heavy metal ions from aqueous solution. It has been well known that chitosan demonstrates the unique adsorption ability towards many metal cations [36]. Now this material attracts growing attention in view of its utilization for removing heavy metals cation from diluted aqueous solution. A great number of chitosan derivatives have been obtained to adsorb metal ions by grafting new functional groups are incorporated with chitosan backbone. The new functional groups are incorporated with chitosan to increase the density of adsorption sites, to change the PH range for metal adsorption and to change the adsorption sites in order to increase adsorption selectivity for the target metal.

The removal of lead ions from aqueous solution is carried out using chitosan/TiO2 hybrid film (CTF) [37]. Langmuir and Freundlich models adequately predicted adsorption of Pb (11) on CTF; however, only the Freundlich equation yielded a better fit. This suggests that CTF has characteristic with several possible functional groups responsible for adsorption of Pb (11). In addition, the parameter K of Freundlich model increased as the temperature increased, so did the amount of Pb (11) adsorbed. The increase in metal uptake with increasing temperature may be due to higher affinity of sites for metal or an increase in the number of binding sites on CTF.

Recently [38] two types of chitosan-coated cation fibers (SCCH and RCCH) were applied to remove and recover Hg (11) ions in aqueous solution at different temperatures. Their results revealed that the adsorption
kinetic process of both fibers for Hg (II) followed the pseudo second order model at lower temperature and the pseudo first order model at higher temperature in the presence of alkali and alkaline earth metals and some heavy metal under optimum conditions.

Biomass: Heavy metal pollution is an environmental problem of worldwide concern [39]. One of the promising techniques for the removal of the metals is the use of living or non living organisms and their derivatives. Indeed, a wide variety of microorganisms (both living and non viable) have been found to be capable of sequestering trace levels of metal ions from dilute aqueous solutions to ppb level. The non viable forms have been proposed as potential sorbents, since these are essentially dead materials, which require no nutrition to maintain the biomass and the need to provide suitable growth condition also do not arise. One of the most promising types of biosorbents is marine algae biomass (seaweed), in view of their high uptake capacity as well as the ready abundance [40, 41].

A wide variety of biomass is being considered as adsorbent of heavy metals for treatment of industrial and domestic wastewaters as well as natural waters, including drinking water. Three types of mulch, cypress bark (C), hard wood bark (H) and pine bark nugget (P) were selected as potential sorbent, to capture heavy metal in urban run off [42]. The hard wood bark mulch had the best physicochemical properties for adsorption of heavy metal ions. In addition, because of the fast removal rate and acceptably high capacity for all the heavy metal ions, it was concluded that the hard wood bark mulch is the best of the three adsorption for treatment of urban run off containing trace amounts of heavy metals. At pH 5 and 6, the Langmuir constants (m) for each metal were found to be 0.324 and 0.359 mmol/g (Cu); 0.306 and 0.350 mmol/g (Pb); and 0.185 and 0.187 mmol/g Zn at 25 °C. Table 4 summaries the comparison of the maximum adsorption capacities for various adsorbents including the cross-linked grape waste gel [43]. This Table shows that the polyphenol-containing adsorbents such as mimosa tannin (condensed tannin) [44] and persimmon tanning[45] have higher adsorption capacities than other biomasses such as sugarcane bagasses [46] and chitosan [47,48]. The grape waste gel containing the polyphenolic groups also demonstrated a high adsorption capacity for Cr (VI) comparable to those of other tannin containing gels. However, compared to other gels, the preparation process of the grape waste gel is simple and economical because the feed material is grape waste itself whereas other tannin gels are produced from expensive pure tannin compounds. Therefore, the utilization of this biomass for the preparation of a more sophisticated adsorbent for Cr (VI) ions for environmental remediation looks highly promising.

Natural Sorbents
Zeolite: Zeolites are micro porous crystalline solids with well defined structures. Naturally occurring zeolites are hydrated aluminosilicate materials with high cation exchange capacity[10]. Sorption of arsenic on natural zeolites has been studied extensively in recent years due to their low cost and availability in nature [49, 50]. Natural mordenite (NM), natural clinoptilolite (NC), surfactants modified natural mordenite (SM NM) and surfactant modified natural clinoptilolite (SMNC) have been proposed for the removal of As (V) from aqueous solution. The pseudo-first order rate constants (K) are 1.06 and 0.52 /h for 1 and 0.5 g of SMNM respectively. The observed k values 1.28 and 0.7 /h for 1 and 0.5 gm of SMNC respectively are slightly high as compared to SMNM. Surfactant surface coverage plays an important role and a significant increase in As (V) sorption capacity could be achieved as the surfactant (HDTMA) loading level on zeolite exceeded monolayer coverage. At a surfactant partial bilayer coverage, As(V) sorption capacity of 97.33 and 45.33 mmol/Kg derived from Langmuir isotherm for SMNM and SMNC, respectively, are significantly high compared to 17.33 and 9.33 mmol/Kg corresponding to NM and NC.
Table 5: Freundlich adsorption isotherm parameters for Cd adsorption on Zeolite, Pumice and Vermiculite (52)

<table>
<thead>
<tr>
<th>Adsorbents</th>
<th>( K_f ) (mg/L)</th>
<th>( n )</th>
<th>( R^2 )</th>
<th>( p )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite</td>
<td>0.65</td>
<td>0.36</td>
<td>0.999</td>
<td>0.06001</td>
</tr>
<tr>
<td>Pumice</td>
<td>0.55</td>
<td>0.32</td>
<td>0.985</td>
<td>0.06001</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>0.69</td>
<td>0.32</td>
<td>0.999</td>
<td>0.06001</td>
</tr>
</tbody>
</table>

A study was conducted to modify the adsorption characteristic of natural Zeolites using iron or manganese or both iron and manganese compounds to adsorb arsenate from water considering the experimental conditions to obtain the different metallic-modified zeolites [51]. The modified clinoptilolite-heulandite rich tuffs were characterized by analysis. The elemental composition and the specific surface area of the zeolite material were also determined. The arsenate adsorption by the modified zeolite was carried on in a batch system considering a contact time from 5 min to 24 h for kinetic experimentation. In general, the results suggested that the kinetic adsorption of arsenates on the modified clinoptilolite-rich tuffs depend of the metallic species that modified the surface characteristic of the zeolite material, the chemical nature of the metal as well as the association between different metallic chemical species in the zeolite surface. Batch experiments were conducted to study the sorption of Cd in three different minerals; vermiculite, zeolite and pumice [52], natural pumice from lipari has high silica content and is thus a hard and highly abrasive material. The Freundlich adsorption capacity, \( n \), for Zeolite, pumice and vermiculite showed similar values (Table 5) and this exponential term controls the "curvature" of the isotherm. Moreover, the Freundlich constant, \( n \), can also be considered a measure of the deviation from linearity of the adsorption. Values of \( n \) were less than unity, which suggests that an increased adsorption can modify the sorbent and that a chemical rather than physical adsorption was dominant. The \( K_f \) values were in the order of vermiculite > Zeolite > pumice and this is imputable to different adsorption affinities of mineral surfaces.

Clay and Modified Clay: Clay is naturally occurring material composed primarily from fine grained minerals, which show plasticity through a variable range of water content.

Phosphate clay [53] characteristically has a high content of apatite up to 24 to 32% of total dry weight. Which is too fine to recover during processing? In addition, phyllosilicate minerals (mainly smectite, polygorskite and kaolinite constitute a major fraction of phosphate clay. This clay has a high cation exchange capacity (CEC) and neutral to slightly acidic pH. These properties suggest that addition of phosphatic clay as a binding agent to immobilize heavy metal could be a cost-effective approach for the remediation of soils, sediments and water contaminated with heavy metals. Any clay of volcanic origin as compared with other clay types, it has excellent adsorption properties and passes adsorption sites available within its interlayer space as well as on the outer surface and edges. A composite adsorbent [54], manganese oxide coated with bentonite (MMB), was proposed and studied for removal of Cu (11). Relative to iron or aluminum oxide, manganese oxide have a high surface area, should provide an efficient surface for the manganese oxide. At the same time, the manganese oxides can improve the metal adsorption capacity of bentonite. Langmuir monolayer adsorption capacity of MMB (105,38mg/g) was found greater than that of the raw bentonite (42.41mg/g). Comparison between sorption of Pb (II) on to phosphate modified and unmodified clay were studied [55]. The adsorption reaction on both adsorbents was found to be chemically activated reaction with energy of activation, at 500 mg/l of Pb (II) in solution was 19 and 10.68 kg/mol for phosphate modified and unmodified adsorbents, respectively. The values of thermodynamic parameters of adsorption suggest an endothermic, spontaneous and an increase in randomness at the solid-liquid interface. The effectiveness of phosphate clay, a by-product of the phosphate mining industry, for immobilizing heavy metals; Pb (II), Cd (II) and Zn (II) from aqueous solution was investigated by Singh et al. [2]. The amount of metals sorbed on to phosphatic clay decreased in the order Pb (II) > Cd (II) > Zn (II). Equilibrium and thermodynamic studies of the removal of Cd by adsorption on indigenous clay have been investigated [56]. Effect of temperature and thermodynamic parameters confirm the process of removal to be endothermic in nature. The removal decreased from 80.3% to 51.3% by increasing the temperature from 30 to 50 °C.

Calcite and Hydroxyapatite: The development of new products which are abundant in nature, low in cost and have minimal environmental impact for restoration of natural resources is an important area of material science
Calcite and hydroxyapatite fulfill both characteristics and have potential to retain heavy metals from industrial effluents. A characterized commercial samples of calcite (CA) and hydroxyapatite (HAP) were compared for sorption of Cd, Zn and Co. Results show that the affinities of the studied heavy metal for calcite and hydroxyapatite follow the sequence: Cd > Zn > Co and Cd > Zn = Co, respectively. Retention increased with P_Ca and pH and could be modeled by: (a) a non-ideal ion exchange mechanism (Me/Ca) for the adsorption of Cd, Zn and Co onto CA; and (b) a mechanism of non ideal ion exchange and specific adsorption (Me/Ca and PO_4-Me) in the case of HAP. The PH dependence is indirect in CA and is related to its solubility changes (P_Ca increases with PH and so does sorption of Cd, Zn and Co). However, calcite has better performance for water treatment due to its greater efficiency for the retention of Cd, Zn and Co (over two order of magnitude per gram of material) and its lower solubility in a wide ranges of pH(6-9).

**Modified Cement:** Adsorption removal of actinide and lanthanide ions from aqueous solution using modified synthetic humic acid magnesia cement was investigated [58]. The results showed that the pore diffusion is the rate limiting for the metal ion studied and the prepared synthetic sorbent (HF-2) can be used for removal of actinide and lanthanide ions from waste water. Improved sorption capacity of ion exchange resins may have advantages over non-specific adsorbents. Adsorption on cement is a promising technique for this purpose. The potential use of sorrel's cement was modified by the introduction of iron in its structure (MF-1) to increase its chemical stability and strength as well as its adsorption capacity. It is found that this material is suitable for use in immobilization of nuclear waste in cement matrix.

**Sorbents for Radionuclide:** The discharge of the radionuclide by patients or of un used radioactive substances as a waste to the environment can cause serious radioactive problems [59]. The precautions to reduce this problem are to keep the liquid wastes in lead tanks and the solid wastes in lead chambers until their radioactivity level reduces to an allowable value to discharge in to the environment. This method is expensive, cumbersome and far away being practical and avoiding the harmful effect of radioactivity. Moreover, this method can not provide a complete shielding for radioactivity besides the tanks or chambers occupy large areas. Finally the diluted radionuclide is left to the environment before their activity is reduced to a harmless level. In addition to the radioactive contamination, it causes heavy metal contamination and poisoning because radionuclide converts to stable metal ions in their steady states. When they mix with underground water their harmful effects become unavoidable. Therefore, the removal of these ionized radioactive substances from liquid wastes is of vital importance. There are various ways of removing these ionized species from wastewater such as reverse osmosis, ion-exchange, precipitation and coagulation. However, these methods quite expensive and are not so effective. One of the most important practical methods for treatment of radioactive waste is adsorption. The use of sorbents to remove radionuclide has some advantages over the other methods. Cr-51 radionuclide used in nuclear medicine was removed by the use of water plants such as Eichhornia crassipes, pista Sp, Nymphaea alba, Menhita aquatic, Ephorbia sp. and lemma minor as adsorbents [60]. Many researchers used adsorbent for treatment of radioactive wastes such as soil [61,62], kaolinite [63,64], Humic substances [65], goethite-coated sand [66], activated carbon [67] and fibrous waste tea [59]. The experimental data for adsorption of Tl-201 on fibrous waste tea showed an excellent agreement with theoretical kinetic constants for different pH values as shown in Table 6. The R^2 values are very high, which are between 0.9998 and 1.0.

**Micro-particle Adsorbents:** Biomass generated as a by-product of fermentative process offers a great potential for adopting an economical metal-recovery system [10].
Biomass of Spergillus niger, Penicillium chrysogenum, Rhizopus nigricans, Aspergillus nodosum, Sargassum natans, Chlorella fusca, Oscillatoria angustissima and Streptomyces Sp, have highest metal adsorption capacities ranging from 5 to 641 mg/g mainly for Pb, Zn, Cd, Cr, Cu and Ni. The efficiency of a new process for wastewater treatment by adsorption onto micro-particles of dry plant was studied. These microparticles are obtained from grinded and dried coriobrotus elulis plant. The removal percentage of heavy metals from industrial waste water by C. edulis particles was 94% for Cd(II), 91% for Cu(II), 99% for Pb(II) and 98% for Zn(II). The maximum adsorption capacity was depending on the type of ion (atomic weight, ionic radius and structure, ...), many researchers look for sorbents issued from agricultural and forestry source, such as peumaria lobate ohvi [68], sugar beet pulp [69], Echroina speciosa (Nile rose) [70] and capressus semprevirens, Eucalyptus longifolia and pinus halopensis [71] for removal of heavy metal ions.

Miscellaneous: Adsorption characteristics of heavy metals: Cu(II), Pb(II), Zn(II) and Cd(II) ions on tourmaline were studied [72]. Tourmaline was found to remove heavy metal ions efficiently from aqueous solution with selectivity in the order of Pb > Cu > Cd > Zn. The maximum heavy metal ion adsorbed by tourmaline was found to be 78.86, 154.08, 67.25 and 66.67 mg/g for Cu, Pb, Zn of Cd respectively. The temperature (25-55°C) had a small effect on the adsorption capacity of tourmaline. Competitive adsorption of the studied heavy metal ions was also studied. Sorption profile of Cd (II) ions on to beach sand from aqueous solution followed first order rate equation [73] and sorption capacity $Q_{m}=46.91$ mmol/g.

Comparison of Sorption Performance: The comparison of the maximum adsorption capacities for various adsorbents were summarized in Fig. 1 [15]. It is evident from our literature and Fig. 1 that some low-cost adsorbents such as chitosan, zeolites, waste slurry and lignin have demonstrated outstanding removal capabilities for heavy metals, which is far better than commercial sorbents. Most toxic heavy metals such as Co, Zn, Cd and Hg ions, for instance, have been effectively removed by chitosan, which performs significantly better than any types of CAC in terms of metal loading capacities. Chitin, one of the natural zeolite, is a good low-cost adsorbent for Cd and Pb removal. Waste slurry is another adsorbent that is able to remove Cr, Pb and Hg ions effectively from aqueous solutions at low-cost. As for Cr (VI) removal, the adsorption capacity of waste slurry is the highest among other low-cost adsorbents and is nearly four times higher than that of CAC. Lignin is considered as the best low-cost adsorbent for Pb and Zn removal. It adsorbs Pb nearly two times higher than waste slurry and its removal capability for Zn is comparable to that of chitosan. Even its adsorption capacity for Pb (II) is significantly more than 30 times higher than that of CAC.

Sorption Mechanism: The sorption of metal from solution is not necessarily a simple process involving a single species [2]. In most cases, more than one species is being adsorbed in to more than one type of surface site during
the sorption process. Identifying the sorption mechanisms of heavy metals by sorbents is important to predict its efficiency from heavy metal immobilization in the contaminated soil and sediment environment.

The mechanism of sorption of heavy metals often involves the chemical reaction between the functional groups on the sorbent and the metal ions, or cation-exchange reaction due to the high cation-exchange capacity (CEC) of the sorbent [74]. Some other mechanisms may also be involved such as transport in the bulk of liquid phase, diffusion across the liquid film surrounding the solid particles and diffusion in macropores or micropores. The chemical reaction for the adsorption of metal onto a solid substance is described by [18]:

$$M + S \rightarrow MS$$

Where M is the metal, sorbate, S is the solid, sorbent and MS is the metal-solid sorbent complex. On the surface of the sorbent primarily the sorption follows two mechanisms, chemisorption and physical adsorption. The amount of sorbate that sorbent can accumulate is a key parameter for process engineering design. This capacity is determined by generating an equilibrium sorption isotherm. Singh et al. [2] concluded that in addition to metal-phosphate formation several other possible mechanisms may have contributed simultaneously to heavy metals removed by phosphatic clay, including surface complexation, ion-exchange, diffusion and precipitation of metal carbonate. The significant differences between the amounts of metals desorbed from phosphatic clay suggest differences in their sorption mechanisms. Biosorption of heavy metal by non-living biomass of microbial or plant origin is an innovative for removal of these pollutants from aqueous solution. Due to unique chemical composition biomass sequesters metal ion by forming complexes from solution [75].

X-ray photoelectron spectroscopy(XPS) and fourier transform infrared spectroscopy(FTIR) studies of adsorption of heavy metal on biomass of padina sp. and sargassum sp. before and after adsorption indicated similar chelating characteristics of metals (Pb, Zn, Cd, Cu and Ni) coordination to the functional groups in the cell wall of the biomass. The functional groups involved in bivalent metal biosorption included carboxyl, ether, alcoholic and amino groups. Sulphonate groups did not played a major role in the binding of bivalent ions [39].

**Multicomponent Heavy Metals Sorption:** Given the adsorption of heavy metals in real system involving more than one component [13], adsorption equilibrium engaging competition between molecules of different types is warranted for better understanding of the system and design purposes. In contrast, only a few isotherms were developed to describe equilibrium in such systems. Selectivity sequences for heavy metal cations in seven Brazilian soils with different chemical and mineralogical characteristics were evaluated. The distribution coefficients ($K_d$), was related to valence they did not exactly follow the order of electronegativity of the metal cations [76]. For individual elements, consideration of the Morsno softness parameter and hydrolysis properties of the heavy metal cations improves prediction of the final sequences. The most frequent heavy metal cation selectivity sequences were $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd} > \text{Zn} > \text{Ni} > \text{Pb} > \text{Cr} > \text{Cu} > \text{Cd} > \text{Ni} > \text{Zn}$.

Aksu et al. [77] studied the biosorption of Cr (VI) and Ni (II) onto dried activated sludge. They noticed that the co-ion effect on the equilibrium uptake became more significant as their concentration in solution is increased along with the pH rise for Cr (VI) and (pH) reduction for Ni (II). In their study, multicomponent Freundlich model with parameters acquired through non-linear regression can well-fit the experimental results at different initial mixture concentration range and pH values. Cay et al. [78] examined single and binary component adsorption of Cu (II) and Cd (II) from aqueous solutions using tea-industry waste. Equilibrium uptake of cadmium (II) and nickel (II) is improved by incrementing its initial metal ion concentration up to 150 mg/L. In contrast, the presence of increasing concentrations of other metal ions brought about the deterioration in equilibrium uptake value. In turn, binary biosorption of Cd (II) and Ni (II) onto dried Chlorella vulgaris was investigated by Aksu and Donmez [79]. Biosorption data in their binary systems showed that the adsorbed amount of one metal declines as the concentration of other competitive metal in the solution increases. The consequence is quite substantial for Ni (II) biosorption as the sorption process is strongly suppressed in the presence of higher Cd(II) concentration in solution.

**CONCLUSIONS**

This review shows that the study on low-cost adsorbents for heavy metal removal has attracted the attention of more scientists. Natural, industrial wastes, Agricultural and micorsorbents were found to be good...
alternative low-cost adsorbents to CAC for removal of heavy metals such as Pb, Cr, Cd, Ni, Zn, As, Hg, Cu, Ag from contaminated water. A few adsorbents that stand for high adsorption capacities are chitosan, Clinoptilolite, zeolite, waste slurry and lignin. The low-cost adsorbents may contribute to the sustainability of the surrounding environment. Undoubtedly, low-cost adsorbents offer a lot of promising benefits for commercial purpose in the future. Pseudo-first and-second order rate expressions have been and still in wide-use for studying the sorption of heavy metals from aqueous solutions.

REFERENCES


