CHAPTER 2

LITERATURE REVIEW

Leonardite exhibit unique sorption, ion-exchange, complex-forming and other properties that have been, the sorption capability of leonardite towards metal cations have been done by Horacek et al., in 1994. The utilization of leonardite pre-treated (loaded) with Ca^{2+} ions for remove heavy metal cations from wastewaters was investigated [68]. It was demonstrated that the coal-based materials can be used for a low-cost ion exchanger alternative. It was found that the calcium-load form of the two types of brown coals (leonardite and peat) can be effectively used for copper, zinc and lead removal by ion exchange of the calcium.

Various researches on leonardite were intensively investigated. In 1999, Leland et al. used a crude leonardite humic acid (LHA) for removal of the organic and inorganic test pollutants, applied singly and as mixtures. The former include pyrene, difenzoquat, and rhodamine B base, whereas the latter were consisted of Pb^{2+}, Zn^{2+}, Ni^{2+}, Cu^{2+}, Sr^{2+}, Cd^{2+}, As^{3+}, Ag^{+} and Mg^{2+}. The LHA form was dissolved in water for batch precipitation by using commercial lime as the coagulant, and packed as a solid for the continuous column extraction. It was found that the precipitation of lime/LHA system is most effective for complete metal removal. All precipitated material (including metal hydroxides and organics) was incorporated in the sludge formed, especially in the case of $Sr(OH)_2$ cannot removed by simple liming, but be able to remove by lime/LHA system. Pyrene and difenzoquat were also removed, whereas rhodamine B base was not. For the column extraction, the removal of three organic compounds was carried out, including those containing mixed contaminants. As for metals, the column showed the most effectively for Pb^{2+}, Cu^{2+} and Sr^{2+} removal [69].

Moreover, the interaction between leonardite and divalent metals was investigated. Sole et al. (2002) studied the adsorption of zinc on leonardite from Torrelapaja, Spain and studied the factors that affected the adsorption such as a function of pH, contact time and concentration of metal solutions. It was observed that, the adsorption capacity of 27.2 mg of Zn^{2+}/g leonardite was achieved at pH of 6.0. The prominent point in this cast is the adsorbent, leonardite, was used in its crude from without previous treatment [7].

In 2004, a further investigation on the use of twelve carbonaceous materials for adsorption copper, cadmium and silver from aqueous solutions was conducted, by Hanzlik et al. [70]. For the twelve materials were spruce wood, pine bark, cork, peat, and coals of different degree of coalification namely, brown coals: fusinite, lignite and leonardite. Other studied materials were bituminous coal, anthracite, and the industrial carbon-rich materials: coke, activated carbon F-400 and $Multisorb_{TM}$ 100. It was observed that, all the studied materials were differ in their degree of coalification, elemental composition, surface oxygen groups content, and structural properties. Biological materials (spruce wood, pine bark and cork) showed a very slow affinity for adsorption of metals. Because of the low COOH content and low BET surface area. Whereas, the best results were obtained for the high content of oxygen- rich materials: lignite and leonardite. In the part of the highly carbonized materials, exhibited low ability to adsorb copper or cadmium, their capacity to adsorb silver was very high. For activated carbon, the physiosorption is adsorption driving mechanism, and another possible mechanism is the precipitate of new phase metal salts, because of an observable increase in pH during equilibrium.

Furthermore, these authors (Hanzlik et al.) studying the adsorption of copper, cadmium and silver from aqueous solutions in the binary and ternary systems, by twelve natural carbonaceous materials, that previous mentioned. Because of the presence of only one heavy metal ion is a rare situation in nature or in wastewaters. It was reported that, for cadmium, the adsorption was decreased by the effect of foreign ions in solution. In contrast, copper and silver can adsorbed much better in binary or ternary mixtures, except of the highly transformed materials, and in the mixtures, the total adsorption of metals was considerably higher than the individual species. The ability of all adsorbents for adsorbed the tested metals was also reported that, spruce wood, pine bark, cork, peat, Multisorb$_{TM}$ 100 and fusinite exhibited the highest affinity for copper. Because of the greatest ionic potential of copper make it the most strongly attracted to the adsorbent. Anyhow, it is unlikely to be so simple for explanation, because of the complex heterogeneous nature of the sorbent, together with the abundance of functional groups present. And the highly carbonified materials displayed the best adsorption capacity for Ag, except for wood and Multisorb$_{TM}$ 100, Cd binding is the worst [71].

In 2005, the adsorption of nickel and copper on leonardite in single and binary systems was studied, to investigate the effect of the presence of one metal on the adsorption of another metal [10]. Furthermore, the influence of calcium ions on the removal of these two heavy metals was also investigated. Because of calcium ions is mostly present in natural waters in the catalonia area (Spain). The results indicated that, the maximum adsorption capacities of leonardite for nickel and copper were 0.26

mmol g^{-1} and 0.33 mmol g^{-1}, respectively, regarding the individual removal of ions. In the case of mixed ions, the presence of nickel has a slightly affect on the removal of copper. However, the removal of nickel decreased by up to 65% by the presence of copper, because of a weaker interaction of nickel with the active groups on the leonardite surface as compare with copper. Concerning copper has the higher ionic potential (2.89) compared with nickel (2.50), and then leading to the high adsorption capacity. The presence of calcium ions affected the removal of copper and nickel by leonardite, found that the sorption of nickel was more affected particularly at low concentrations, might be due to calcium ions competing more effectively with nickel while the sorption of copper was less affected.

The similar experimental work, demonstrated the competitive adsorption tests of the two heavy metals, cadmium and lead on leonardite, by Lao et al. (2005) [1]. In the individual metal studies, it was point out that pH in range 5-6 was found to be optimum for Cd^{2+} and Pb^{2+} removal, and that the uptake of both metals on untreated leonardite were 50.6 mg g^{-1} and 250.7 mg g^{-1}, respectively. These results showed that Pb^{2+} was retained more strongly than Cd^{2+} by leonardite. Regarding to the basis on ionic properties namely, the electronegativity and the ionic potential of Pb^{2+} are higher than Cd^{2+}. In this case, means that Pb^{2+} interacted more strongly electrostatically with the surface groups present on the surface of the leonardite. Moreover, another factor is the ionic radius of ions, especially a smaller ionic radius implies that more molecules can adsorb onto a fixed surface area of sorbent. As can be seen, their hydrated shell, Pb^{2+} had the smaller radii, whereby it can penetrate into smaller pores, and, therefore, have a large access to the leonardite surface. For the binary systems, found that Cd^{2+} adsorption was more sensitive than Pb^{2+} to the presence of a competitive sorbate. Furthermore, it was observed that the maximum adsorption capacities of Cd^{2+} and Pb^{2+} decreased to 30.6 mg g^{-1} and 118.7 mg g^{-1}, respectively, which related to the ability of these two metal ions to compete for the adsorption site.

The used of untreated leonardite (in Czech Republic called oxihumolite) for removal of heavy metal cations (Cd^{2+}, Cu^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) from water was evaluated, by P. Janos et al. (2006) [8]. And the kinetic models, namely the pseudo-first and pseudo-second order models were also studied, for describe the kinetics of metals sorption on leonardite. It was found that leonardite exhibited an effective sorbent for the removal of heavy metal cations from water, especially for Pb^{2+}ions, but rather low in the case of Co^{2+} ions. These results were observed in a slightly acidic medium at the equilibrium pH in range 3.5 to 4.5. Because of the natural buffering capacity of leonardite. About the results of the adsorption kinetics, the metal sorption was a quite rapid process for all the examined metals that may be characterized by half-times in range from ca. 10 to 80 min. And the both kinetic models, pseudo-first and pseudo-second-order can explained adequately the metal sorption, although a slightly better fit to the experimental data was achieved when the pseudo-second-order model was used. It was also found that the intraparticle diffusion was the main mechanism controlling the rate of metal sorption. Moreover, various extraction and digestion tests were applied to the sorbents loaded with selected heavy metal cations (Cd^{2+}, Cu^{2+}, Pb^{2+} and Zn^{2+}), for evaluate potential risks associated with the spent sorbent, found that the heavy metals retained most strongly in the loaded sorbents that may be hardly liberated into the environment.

J. Mizera et al. (2007) prepared the low-cost sorbent, chitosan combined with humic acid from leonardite, by using chitosan as a supporting sorbent. To improve the performance of coal sorbents, by prevented the release of humic acid from coal and related to the inadequate stability of coal particles in neutral and alkaline solutions. These authors considered that chitosan can prevent degeneration of the sorption ability probably via removing the humic substances complexes from solution by formation of an insoluble complex. Moreover it was also investigated the potential of this adsorbent on the removal of cesium, cobalt and europium. The effect of chitosan addition was negligible at sorption of Cs. In contrast, it improved sorption efficiency in the case of Eu and Co at neutral pH [72].

Furthermore, the removal of toxic organic substances from water by using leonardite was also investigated. In 2006, research on the adsorption of polycyclic aromatic hydrocarbon (PAHs) using leonardite was carried out, by C. Zoraida et al. [73]. Several PAHs were selected including fluorine (FLE), pyrene (PYR), B*(k)*fluoranthene [B*(k)*F], B*(a)*pyrene [B*(a)*P], and benzo*(g,h,i)*perylene [B*(g,h,i)*P]. Because it is a problem, mainly when they are present in low concentrations, and the abundance of them in contaminated water, sediments and soils. And the importance factors such as pH, contact time and equilibrium adsorption were studied, for determine the capacity of leonardite as the sorbent. It was reported that the pH did not significantly affect the adsorption of PAHs, in the case of PYR, [B*(k)*F], [B*(a)*P], and [B*(g,h,i)*P], by leonardite, except for FLE. Because the former are very chemically inert, by means of the bond linkages are highly stable, and do not have ionizable groups that can be influenced by pH. For the latter compound, the adsorption was higher at lower pH values.

The equilibrium data were fitted to Freundlich isotherm, which is the most widely used to describe the sorption of hydrophobic organic compounds, (HOCs). By determined the water-leonardite partition coefficient, log K_{oc}. It was found that the highest adsorption capacity were B*(g,h,i)*P, showing log K_{oc} equal 4.44, while FLE and B*(k)*F reported the lowest log K_{oc} 4.19 and 4.29, respectively. For B*(a)*P and PYR, the log K_{oc} were 4.36 and 4.37, respectively. The aromaticity of PAHs was the main mechanism that controlled the removal process, and the interaction between the PAHs and leonardite. Moreover, the change of the polarity of humic substances in leonardite may also affect the adsorption capacity.

For another organic pollutant, dyes and pigments, they are considered to be toxic and carcinogenic substances. Furthermore, it is difficult to remove dye materials because they are very stable to light and oxidation reactions. The removal of dye materials by the adsorption process using oxihumolite or leonardite was studied in 2005 [5]. P. Janos et al. studied the adsorption of basic (Methylene Blue and Malachite Green) as well as acid (Egacid Orange and Midlon Black) dyes onto leonardite. The adsorption capacities were estimated from the parameters of the adsorption isotherms, and the factors that affect to the sorption such as pH, the presence of inorganic salts and surfactants were also investigated. It was found that the maximum adsorption capacities ranged from 0.070 mmol g^{-1} (for Midlon Black) to 0.278 mmol g^{-1} (for Malachite Green). For the effect of NaCl on the dye sorption, mainly of the dyes tested, the sorption increased. However, the sorption of Midlon Black was suppressed, probably because of a competition between the salt anions and the anionic dye. Non-ionic surfactants and surfactants that have the same charge as the dye exhibited a slightly affect on the dye sorption, but the oppositely charged surfactants promoted the dye sorption.

Moreover, the effect of pH on the dye sorption was also studied. Decreasing in the acid dye sorption when pH increased, due to some functional groups of humic substances were dissociated, then a negative surface charge increased preventing the sorption of acid dyes. In the case of basic dyes, the pH changed was only minor effect. And it was found that leonardite was suitable for apply in the treatment of neutral or acid wastewater. Because of occurring the dissolution of sorbents when it presence in alkaline solutions.

Furthermore, iron humate (IH) was prepared by P. Janos (in 2003) for used as a new low-cost sorbents to remove basic dyes (Methylene Blue, Methyl Violet, Crystal Violet, Malachite Green and Rhodamine B) from aqueous solutions [74]. IH was prepared by a precipitation of humic acids with an aqueous solutions of iron(II) sulfate. The effect of pH and the factors influencing the adsorption such as the presence of inorganic salts or surfactants were also studied. It was found that, for the selected dye Methylene Blue, pH and the presence of inorganic salts have only slightly effects on the sorption, whereas the dye sorption onto IH increased dramatically in the presence of sodium dedecyl sulfate (SDS).

In 2007 [19], the kinetics of the adsorption of basic dyes (Methylene Blue, Malachite Green, Rhodamine B and Crystal Violet) as well as acid dyes (Egacid Orange, Egacid Yellow and Midlon Black) on leonardite was investigated, by using the pseudo-first and pseudo-second order models for description. However, the applications of leonardite as a sorbent require a more detail about the mechanism of the adsorption. Then the intraparticle diffusion model was used to verified diffusional processes affecting the rate of the dye sorption. It was observed that the adsorption rate of dye was rapid at the initial stage, and gradually decreased until approach the equilibrium time. Malachite Green displayed faster sorption kinetics in comparison with other dyes. Both pseudo-first order and pseudo-second order kinetic models were applied to describe adequately the kinetic dependencies. Although in the case of Malachite Green, the pseudo-second order kinetic models gave a slightly better fit to the experimental data when compare the R^2 values. Moreover, the intraparticle diffusion model was also applied successfully to the examined systems. It was found that the increased dose of the adsorbent and the particle sizes of the adsorbent, results in a decrease of the diffusion rate parameters, while an effect of agitation mode and intensity on the sorption of the selected dyes (Rhodamine B and Egacid Orange) was much less pronounced. Therefore, the diffusion processes inside the particle of the leonardite were identified as the main mechanism controlling the rate of the dye sorption on leonardite.

Overall, the literature review that mentioned previously indicated that leonardite is a good adsorbent for all heavy metals and organic pollutants. It is widely to known that the excellent adsorption behavior of leonardite for heavy metals and organic pollutants removal is attributed to: (1) Focus on an economical aspect, leonardite is a low-cost material, that can used in crude form without pre-treatment, (2) a high content of humic substances in leonardite, and humic acid have many acidic functional groups, mainly carboxylic and phenolic, that are able to bind metal ions, and (3) a high cation exchange capacity of leonardite.