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Review Article

Multicomponent and Competitive Sorption of Heavy Metals- Review on Significant Research and Studies

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Abstract: Heavy metals have acute and chronic effect on human beings and other living organisms also. It is very important to identify the risk and take steps for removal of heavy metals from the effluents. The industries such as paint, pigment, catalyst, fine chemicals, coating, automobile, electronics, battery etc. uses heavy metals in some or other form. They treat the wastewater by using conventional methods. Heavy metal removal from the wastewater by using adsorption is commonly investigated area of research. The wastewater generally contains more than heavy metals. It is envisaged to study the effect of presence of one heavy metal on removal of other heavy metal. It can help selective removal of specific heavy metal and selection proper adsorbent. Most of these investigations indicated that the presence of one metal has significant effect on sorption of other metal. This effect can be positive or negative. Competitive adsorption indicates competition for adsorbent sites. In cooperative mechanism, the presence of one metal has positive effect on sorption of other. The present review intends to study research and studies on the competitive adsorption of heavy metals on different materials.

Keywords: Isotherm, kinetics, concentration, adsorption capacity, uptake, cost.

INTRODUCTION

Heavy metals have tendency to bio-accumulate in human body. Even though the uptake, by means of food is very low, this accumulation aspect makes us to think more acutely about heavy metals. Water resources are getting contaminated with water. The crops, take minerals through water which has mineral impurities from soil. This forms the chain for accumulation of heavy metals. These heavy metals have acute and chronic effect on human beings and other living organisms' also[1-4]. It is very important to identify the risk and take steps for removal of heavy metals from the effluents. The industries such as paint, pigment, catalyst, fine chemicals, coating, automobile, electronics, battery etc. uses heavy metals in some or other form. They treat the wastewater by using conventional methods. The conventional treatment plant contains physical, chemical and biological treatments[5-8]. The removal of organic matter and other specific impurities such as phenol, acetates and other hydrocarbon impurities takes place by chemical and biological treatments. Heavy metal removal is generally carried out using electro-dialysis, precipitation, adsorption, ion exchange, coagulation and floatation[9-20]. Heavy metal removal from the wastewater by using adsorption is commonly investigated area of research[20-26]. The wastewater generally contains more than heavy metals. The effect of presence of one heavy metal on other adsorptive removal of heavy metal need to be studied to make the operation more effective and applicable. The present review intends to study research and studies on the competitive adsorption of heavy metals on different materials.

MULTICOMPONENT AND COMPETITIVE SORPTION OF HEAVY METALS

Rashid *et al*.[27] carried out investigation on chelators-metal interaction in phytoaccumulation of metals.They investigated uptake of cadmium (Cd) and lead (Pb) and their subsequent accumulation in edible tissue of plant. The results indicated that phytoaccumulationan and adsorption of Cd was higher than Pb and copper. Apiratikul *et al*.[28] Carried out investigation on biosorption of binary mixtures of heavy metals. Their investigation was focused on green macro alga, Caulerpa lentillifera. They carried out experiments to study sorption potential of metals namely Cu, Cd, Pb and Zn. Their investigation indicated that, binary adsorption was competitive in nature and the adsorption capacity for any single metal decreased by 10-40% in the presence of the others. For the algae, they found that adsorption capacity decreased by 30-50 percent in presence of other metals. In contrast to this this general statement, they observed that the adsorption of mixtures of Cd and Cu, and of Pb and Cu did not show a reduction in the total adsorption capacity.

Futalan *et al*.[29] Carried out an investigation on Copper, nickel and lead adsorption on chitosan-immobilized on bentonite.The system under their study was a ternary system. They investigated various operating parameters. They found that the adsorption followed pseudo second order kinetics. They predicted that rate determining step was chemisorption. Also the study indicated that nickel removal followed Langmuir model while other two metals followed Freundlich equation. Regeneration studies indicated that HCl provided the highest desorption capacity but with most material damage. Zemanova *et al*.[30] carried out investigation on competitive sorption of Cd, Cu, Pb and Zn[30]. For adsorption experiments he used three types of soil. A Gleyic Fluvisol, a Gleyic Cambisol, a Chernozem were the soils used by them in the experiments. Their results indicated that sorption from single-metal solution was more effective than sorption under multi-metal conditions. Only the Pb sorption was not affected. Non-linear Freundlich equation described the isotherm of the metal uptake. Ramsenthil and Meyyappan carried out investigation on single and multicomponent sorption of copper and zinc ions on Microalgal Resin[31].Their investigation also suggest that there exist a competitive adsorption for the binary mixture solution. Langmuir and Freundlich model in the applied concentration ranges were adequate to describe the uptake. Cu was better adsorbed metal of the two. Compared to single metal sorption, they found that sorption processes were slower in multi-component systems. Competitive adsorption of lead and cadmium was investigated by Al-Malack

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et.al.[32] They used activated carbon (AC) produced from municipal organic solid waste. They also investigated factors affecting adsorption such as pH, contact time, metal concentration and adsorbent dosage. According to these studies, a pH value of 5 and a contact time of 120 minutes were optimum conditions for adsorption. Decrease in removal efficiency and increase in adsorption capacity was observed by them with increase in initial concentration. For cadmium concentration of 100 mg/l, they found 68.3 percent decrease in adsorption for increase in lead concentration from 25 to 300 mg/l. They also observed that non-linear Freundlich adsorption isotherm and pseudo-second-order kinetic models described the uptake of both the metals. Singh and Gupta carried out investigation on sorption of heavy metals[33].Their study indicated that most of the investigations included the isotherm and kinetics of metal uptake. Also competitive adsorption also was being investigated. Most of these studies indicated adsorption as significant unit operation in metal removal with huge potential.

Zeolite was used for competitive adsorption of heavy metals by Shaken *et al*.[34] They carried out investigation on the removal of heavy metals namely cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb) and zinc (Zn). They determined percentage sorption and distribution coefficients. They observed that Freundlich model described the sorption of metals satisfactorily. Percentage removal of 32, 75, 28, 99, and 59 % of the added Cd, Cu, Ni, Pb and Zn was obtained by them. Adsorption and distribution coefficient followed the trend Pb > Cu > Zn > Cd > Ni. Mishra carried out studies on adsorption and desorption of heavy metals[35]. They reviewed some valuable work carried out in recent past. They summarized studies on adsorption of metals on some unconventional and conventional materials such as such as teak tree bark powder, rice husk, natural bentonite, different algae like Ecklonia maxima, Escherichia coli, Ascophyllum nodasum, Rhizopus nigricans, Chromosorb 102 resins and poly(m-phenylenediamine), Cladophora fascicularis, goethite and soils of three nuclear power plant and artificial materials such as Fe oxide-coated sand, goethite pretreated with phosphate, dithizone modified sodium trititanate whisker, modified nanometre sized TiO_2.They also discussed investigation on competitive adsorption. They found that, few studies indicated that regeneration and reusability of the adsorbents was retained for three cycles. Competitive adsorption between cadmium and zinc was investigated by Ming *et al*.[36] They found that, in alkaline soil, zinc indicated higher adsorption, which was not that high for acidic conditions. In acidic conditions, for competitive adsorption, cadmium was adsorbed more than zinc; the trend was reversed for alkaline conditions. Nature of oil affected the competitive adsorption. Competitive adsorption of nickel and cadmium was investigated by Ghasemi-Fasaei *et al*.[37]. They investigated adsorption on two soils, an acidic and a basic soil in competitive and non-competitive mode. The Freundlich model was observed to be better than the Langmuir model for the data. Adsorption capacity in basic soil was higher than acidic soil. For basic soil, nickel sorption indicated higher adsorption capacity than acidic one. The studies indicated higher sorption capacities for nickel than cadmium.

Kosa *et al.*[38] used 8-hydroxyquinoline for modification of Multi-walled carbon nanotubes (MWCNTs).On this modified material, they adsorbed heavy metals, Cu(II), Pb(II), Cd(II) and Zn(II) from aqueous solutions. They investigated the factors affecting adsorption such as temperature, pH, ionic strength, metal ion concentration, and competition among metal ions. The competitive adsorption followed the sequence, Cu (II) > Pb(II) >Zn(II) > Cd(II). The desorption studies indicated that most of the heavy metals desorbed at pH 2. Chen *et al*.[39] carried out an investigation on competitive adsorption of many metals. Their investigation was focused on the heavy metals such as lead, cadmium and copper .They used nano-hydroxyapatite in single- and multi-metal competitive adsorption study. They found that the Langmuir isotherm better fits sorption data than the Freundlich equation. They observed that, for the adsorbent, the adsorption of lead was maximum followed by copper and cadmium. According to their studies, the competitive adsorption data of Cd^{2+} and Cu^{2+} cannot be fitted satisfactorily in the Langmuir isotherm for cadmium and copper. For lead it can be used with R^2 value greater than 0.9.Their studies on selectivity coefficients indicated that there was sharp decrease in the selectivity coefficients for adsorption of Cd on nano-HAP in multi-ion system. It resulted in increasing Pb concentration in solution. Ho and Mckay studied competitive adsorption of copper and nickel on peat[40]. Study indicated that copper has a stronger sorptive potential. Coffee waste was used for competitive adsorption of Cu(II) and Zn(II) from binary heavy metal solutions[41].The adsorbent had higher affinity for copper. The study indicated that the percentage of adsorption of Cu and Zn decreased with increase in the initial metal concentration. The found that, copper ion adsorbed from the single Cu and the binary Cu solutions were very close. On the contrary, for zinc, adsorption went down from 55% from the single metal solution to 8% from the binary solution. El-Eswed *et al.*[42] used Kaolin/Zeolite Based- Geopolymers for sorption of Cu(II), Ni(II), Zn(II), Cd(II) and Pb(II).For kaolinite, they learnt that the adsorption was cooperative, that means it increased with competition. The sorption capacity of zeolite Cd(II), Ni(II), Zn(II) onto geopolymers decreased with competition. They also observed that adsorption of Pb(II) onto geopolymers was not affected significantly by competition.

Maize cob and husk were used to study competitive and non-competitive adsorption of heavy metals by Igwe *et al.*[43].The metals adsorbed were Zn (II), Cd (II) AND Pb (II) ions. The study reiterated that adsorption efficiency of each metal ion was influenced by the presence of other metal ions. Khalfa *et al*.[44] used natural and activated clay as an adsorbent for competitive removal of heavy metals[44].The rate determining steps were intraparticle diffusion steps. They also observed that the pseudo-second-order model described the adsorption. They also observed an increase of the adsorbed quantities of lead and zinc in single and binary systems due to treatment of natural clay with sulfuric acid. This treatment created more active sites and increased the surface area. Their studies on competitive adsorption indicated that the uptake of lead was inhibited in the presence of 10 mg/L of zinc. Zinc was more readily adsorbed than lead. Mourid used Calcareous soils for removal of heavy metals such as lead, cadmium and nickel[45].They observed that the adsorption can be divided in three stages namely rapid, intermediate and steady. First two hours are critical and in this period rapid removal occurs. In intermediate stage the decrease in the sorption with time is observed. These metals were adsorbed in the sequence Cd > Pb >Ni. Activated carbon from Nigerian bamboo was used for adsorption of heavy metals by Ademiluyi and Nze[46]. They carried out investigation on competitive adsorption of nickel, copper, zinc, lead, cadmium and chromium. They found that the bulk density, iodine number, Benzene adsorption, methylene adsorption, and ash content of the activated carbon produced by them were comparable with commercial adsorbents. The adsorption occurred in the order Pb>Cd>Cu>Zn>Ni>Cr. The order of adsorption was in the order of ionic radius of the heavy metals used.

Ha and Rabo carried out investigation on the competitive sorption of heavy metals, cadmium, copper and lead in soil[47].They carried out experiments with mono, bi-and tri-metal batch test. They established mathematical relationship between concentration of the adsorbent in the liquid phase and the solid phase at equilibrium. The order of selectivity was $Pb^{2+} > Cu^{2+} > Cd^{2+}$. According to them, the co-existence of Pb and Cd reduces their tendency to be sorbed on the soil solid phases. The order of affinity was Cd(II)>Pb(II)>Cu(II). In multicomponent adsorption, they obtained removal of 11.86 mg, 11.23 mg and 16.76 mg per gram of smectite. According to them, it is almost impossible to generalize the order of adsorption. Competitive adsorption of cadmium, copper and lead was investigated by Arpa *et al*.[48].They used northern Anatolian smectites as adsorbent material. Taiwo and Chinyere carried out an investigation on multiple adsorption of heavy metal ions using activated carbon from Nigerian bamboo[49].They carried out simultaneous adsorption of (Cd^{2+}, Ni^{2+}, Pb^{2+}, Cr^{3+}, Cu^{2+} and Zn^{2+}.The Freundlich, Temkin isotherm and Dubinin-Radushke- vich (DRK) isotherm models indicated satisfactory fit for the adsorption. Their studies indicated that there was competition among various metals for adsorption sites. Sangiumsak and Punrattanasin carried out adsorption behavior of heavy metals on oil[50]. Their study showed that the metals were adsorbed in the order Ni>Cu >Zn.

CONCLUSION

The industries such as paint, pigment, catalyst, fine chemicals, coating, automobile, electronics, battery etc. uses heavy metals in some or other form. They treat the wastewater by using conventional methods. Heavy metal removal from the wastewater by using adsorption is commonly investigated area of research. The wastewater generally contains more than heavy metals. The effect of presence of one heavy metal on removal of other heavy metal need to be studied for development of efficient and acceptable process. Competitive adsorption indicates competition for adsorbent sites. In cooperative mechanism, the presence of one metal has positive effect on sorption of other.

The research and studies on the multicomponent and competitive adsorption of heavy metals on different materials are summarized in this paper, which can be great help in future research on heavy metal removal by adsorption or biosorption. All the investigations suggested significant effect of presence of one heavy metal on removal of other. It is important to have proper analysis of the wastewater to know the contents. Then one can select proper adsorbent, which can be effective for the pollutants which need to be removed. Selection of the contact mechanism also plays vital role. The research in the adsorption is normally divided into two parts. Primary batch studies and continuous studies.

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