Review article **Available online** www.ijsrr.org **ISSN: 2279–0543**

International Journal of Scientific Research and Reviews

Heavy Metal Removal from Aqueous Solution Using Zeolite
(A Review)

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ABSTRACT

The removal of pollutants from water and wastewater is a problem that has grown with rapid industrialization. Due to extensive anthropogenic activities such as industrial operation particularly mining, agriculture processes and disposal of industrial waste material; their concentration has increased to dangerous levels. Heavy metals in industrial effluent include nickel, chromium, lead, zinc, arsenic, cadmium, selenium and uranium. Many methods are used for the removal of heavy metals such as ion exchange, reverse osmosis chemical precipitation, electro dialysis, ultra filtration, nano filtration, coagulation, flocculation, floatation etc. But these methods have many disadvantages like high reagent requirement, unpredictable metal ion removal, generation of toxic sludge etc. Adsorption is recognized as an effective and economic method for low concentration heavy metal wastewater treatment. The natural Zeolites could adsorb and remove the heavy metals in the aqueous solutions. This paper reviews the use of synthetic zeolite as an adsorbent for the removal of heavy metals from aqueous solution. The critical parameters affecting the adsorption of heavy metal ions are investigated by utilizing zeolite NaX as the potential adsorbent. The adsorptions of heavy metal ions are strongly dependent on pH, temperature, contact time and initial adsorbate condition. The aim of this study was determining the removal efficiency of zeolite for removing heavy metals from aquatic solutions.

KEY WORDS-

Heavy metal, adsorption, zeolite NaX, adsorbent.

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INTRODUCTION

Water contaminated by heavy metal ions had become much more serious with a rapid development of industries and competitive use of fresh water in many parts of the world[1]. "Heavy metals" is a general collective term applied to the group of metals and metalloids with an atomic density greater than 6 gm^{-3} include such elements as Cd, Cr, Cu, Hg, Ni, Pb, and Zn which are commonly associated with pollution and toxicity problems. These pollutants reach the environment from the vast array of anthropogenic sources as well as natural geochemical process[2]. The release of heavy these metals into the environment through industry effluents is a major concern, worldwide and removal of such pollutants has been a great concern during last decades. These heavy metals are non-biodegradable which leads to several health problems in animals, plants and human beings such as cancer, kidney failure, metabolic acidosis, oral ulcer, renal failure and damage in stomach of the rodent[3,4].Therefore, the removal of heavy metal ions from water has become an important subject today. Several conventional methods exist for the removal of heavy metal pollutants from wastewater. These methods include precipitation, electroplating, chemical coagulation, ion-exchange, membrane separation, and electro kinetics[5]. However, most of these methods have limitations, which include high cost, unavailability, and generation of large volumes of secondary waste and poor removal efficiency. Considering from the economy and efficiency point of view, adsorption is regarded as the most promising and widely used method among all these[6]. The efficiency of adsorption depends on many factors, including the surface area, pore size distribution, polarity, and functional groups of the adsorbent[7]. The selectivity series of clinoptilolite in the sodium form was determined by Zamzow et al., as follows: $Pb^{2+} > Cd^{2+} > Cs^{+} > Cu^{2+} > Co^{2+} > Cr^{3+} > Zn^{2+} > Ni^{2+} > Hg^{2+}$[8]. Zeolites are crystalline alumino-silicates having uniform cavities and having strong ion-exchange capacity. The substitution of aluminium for silicon results in a residual negative charge density, which is balanced by the presence of other metallic ions in the pores of the framework. Due to their structural characteristics, zeolite can be used in several applications[9].

The objective of the present study is to investigate the adsorption potential of on synthetic zeolite in the removal of heavy metal ions from aqueous solution. The effects of pH, adsorbent dosage, contact time and temperature on adsorption capacity of synthetic Zeolite have been investigated. The Langmuir and Freundlich isotherms models are applied to the sorption data to calculate the different parameters and the best fitting achieved**.** The pollution of water resources due to the disposal of heavy metals has been an increasing worldwide concern for the last few decades. The removal of pollutants from water and wastewater is a problem that has grown with rapid industrialization. The discharge of toxic metals into water sources is a serious pollution problem, which may affect the quality of water supply. By confirming the toxic effects of these metals, various methods have been implemented to remove pollutants from aqueous solutions. The aim of this study was determining the removal efficiency of synthetic zeolite for removing heavy metals from aqueous solutions.

TOXIC HEAVY METALS

Pb^{+2}, Cu^{+2}, Fe^{+3} and Cr^{+3} are especially common metals that tend to accumulate in organisms, causing numerous diseases and disorders[10]. They are also common groundwater contaminants at industrial and military installations. Numerous processes exist for removing dissolved heavy metals, including ion exchange, precipitation, phytoextraction, ultrafiltration, reverse osmosis, and electro dialysis[11,12]. Copper is one of the most important metals often found in industrial effluents such as acid mine drainage, galvanizing plants, natural ores and municipal wastewater treatment plants. It is not biodegradable and it travels through the food chain via bioaccumulation[13]. Removal of copper from waste water is crucial and its toxicity for human beings is at levels of 100-500 mg per day[14,15].

SOURCES AND CAUSES OF DIFFERENT HEAVY METALS

Table 1: Sources and toxicological effects of some heavy metals:

Heavy metal	**Sources**	**Causes**	**Guideline value (mg/L)**	**References**
Copper	Making pipes, valves, fitting, coating sand alloys, copper jewellery, copper cooking pots, alcoholic beverages from copper brewery equipment, instant gas hot water heaters, hormone pills.	Mucosal irritation, widespread capillary damage, hepatic and renal injury, central nervous system irritation followed by depression, gastrointestinal irritation, necrotic changes in the liver and kidney.	2.0	16,17

Inorganic mercury	Electrolytic production of chlorine, in dental amalgams, electrical appliances.	Tremorors, birth defects, kidney damage, nausea, loss of hearing or vision, gingivitis, chromosome damage, mental retardation, tooth loss, hypertonia- muscle rigidity, minamata disease.	0.006	17,18
Chromium	Steel and textile industry	Skin rashes, respiratory problems, haemolysis, acute renal failure, weakened immune systems, kidney and liver damage, alteration of genetic material, lung cancer, Pulmonary fibrosis.	0.05	17
Nickel	Production of stainless steel, nickel alloys, effluents of silver refineries, electroplating, zinc base casting and storage battery industries.	Skin irritation, damage to the lungs, nervous system, mucous membranes, dizziness, nausea, vomiting, chest pain, rapid respiration.	0.07	17
Cadmium	Contamination from fertilizers	Kidney and tubular cells damage	0.003	17
Lead	Storage batteries, gasoline additives, ammunition: shot and bullets, solder	Irreversible brain damage, injury to the blood- forming systems, nervous system damage	0.01	17

RESULTS & DISCUSSION

Table2: Data from various studies with the subject "Removal of Heavy Metals from Aqueous solutions"

Adsorbent	Heavy Metal	Removal Efficiency (%)	pH	Adsorption capacity (mg/g)	Contact time (min)	Initial Concentration (mg/l)	Reference
Nanozeolite	Cr(VI)	45	3	14.16	60	1	19
Zeolite NaX	Cr(VI)	44.40	4	6.414	120	10	20
Activated carbon	Cr(VI)	98.10	2	9.00	600	500	21,22
Clinoptilolite	Cu(II)	89.62	4	0.24	75	2.748	23
Scolecite natural zeolite	Cr(VI)	85	6.5	0.75	120	20	24
Agriculture wastes carbon	Cr(VI)	91.75	2	59.23	120	250	25
Natural zeolite zlatokopmine, Serbia	Cu(II)	18.6	7	8.3	200	100	26

Effect of pH:-

pH is one of the most important parameters controlling uptake of heavy metals from wastewater and aqueous solutions. Removal efficiency for natural pH was obtained 15.38% and minimum removal efficiency was 7.69%. In the studies, the percentage adsorption increased with increasing pH to reach a maximum at pH 6 & then, it decreased with further increase in pH[27].

The mechanism of adsorption at the zeolite NaX surface reflects the nature of physicochemical interaction of the metal ions in the solution and the active sites of the zeolite NaX. The uptake capacity of zeolite NaX is found maximum at pH 6.0. The removal of metal ions is strongly dependent on the pH of the solution[28].

Effect of temperature:-

In E. Muzenda et al.'s study, the effect of temperature on adsorption of copper(II) ions was investigated by varying temperature from 30-90^{0}C at various inital concentration at a pH of 4 for 24 hr. and adsorption was found to be temperature dependent. At higher temperature zeolite pore sizes could increase enhancing the rate of intrapartical diffusion of ions[29].

In Pankaj pandey et al.'s study effect of temperature on adsorption of copper (II) ions is studied by conducting different sets of experiment at initial concentration of 25ppm at different temperature i.e. 288,303,323 K. It is observed that adsorption of copper ions increases with increase in the temperature[9].

Effect of Contact Time:-

The percent removal of heavy metal increases by increase of contact time till equilibrium is attained. The removal of copper (II) ions is high in the first 10 min. and then, the rate significantly decreases and eventually approaches zero, and finally the equilibrium point has been attained[30]. From V.O. Vasylechko et al.'s study, the removal of copper (II) ions increased with time and attained saturation in about 60-70 min.[31].

Pankaj pandey et al.'s the removal of copper(II) increases with time and attains saturation in 60-120 min. The removal rate of adsorption is rapid initially but it gradually decreases with time until it reaches equilibrium[9].

The Effect of Initial Concentration of Heavy Metal:-

The effect of initial concentration on removal efficiency that by increasing initial concentration of heavy metal, the removal efficiency decreased. From Samarghandi MR et al.'s study the percentage of Cr(VI) removal decreased from 99.37-40.24% by increasing the initial Cr(VI) concentration from 20 -100 mg/l .the decrease in the percentage removal can be explained by the fact that the adsorbent had a limited number of active sites; which would have become saturated above a certain concentration[32].

The Effect of Zeolite Concentration:-

Adsorption increased with increase in zeolite amount for fixed initial concentration, this is because the increase in zeolite amount leads to increase adsorption surface area and available active sites[33].

ADSORPTION ISOTHERMS

The adsorption isotherms are very important in describing the adsorption behaviour of solutes on the specific adsorbents. In these studies, two important isotherm models such as Langmuir and Freundlich were selected and studied.

Langmuir adsorption isotherm is the most popular and is a two-parameter equation. Langmuir sorption isotherm models the monolayer coverage of the sorption surfaces and assumes that sorption occurs on a structurally homogeneous adsorbent and all the sorption sites are energetically identical. The general form of Langmuir isotherm is as follows-

$$C_e/Q_e = 1/(Q_m b) + C_e/Q_m$$

Where costants b and Q_m relate to the energy of adsorption and adsorption capacity and their values are obtained from the slope and intercept of the plot of C_e/Q_e versus C_e. If the plot is linear it shows that the adsorption follows the Langmuir isotherm. The value of b, which is a measure of heat of adsorption, is utilized to calculate dimensionless separation parameter R_L[34].

The Freundlich expression is an empirical equcation based on a heterogeneous surface[35]. This isotherm is the earliest known relationship and described by the following equcation:

$$\text{Log } Q_e = \log K + 1/n(\log C_e)$$

Where K and n are Freundlich constants which correspond to adsorption capacity and adsorption intensity respectively. The slope (1/n) and intercept (K) of a log-log plot of Q_e versus C_e are determined.

CONCLUSION:-

From various studies we concludes some results which are as follows –

1) The removal efficiency is increased with increase in pH. The maximum of removal efficiency was occurred at pH 6 and then, it decreased with further increase in pH.
2) Adsorption of ions increases with increase in the temperature.
3) With increasing time to reach equilibrium time, the removal efficiency was increased.
4) Percentage removal of ions decreases with increase in initial metal concentration.

According to these results, it can be concluded that the zeolite is a good absorbent for removal of heavy metals ions from aqueous solution.

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