Application of Appopolite in Adsorption of Heavy Metals (Co and Ni) from Waste Water

Rohini Singh[1*],Kavita Kulkarni[2], A.D.Kulkarni[2]

1. M.Tech Student, Department of Chemical Engineering, BVDU, Pune, India

2. Associate Professor, BVDU College of Engineering, Pune, India

   Bharati Vidyapeeth Deemed University, College of Engineering, Pune, 411043, India

* E-mail- richarohini@yahoo.co.in

E-mail- kskulkarni@bvucoep.edu.in

Abstract

The optimum conditions for adsorption/ion exchange by using a batch method were evaluated by changing various parameters such as adsorbent amount, initial pH of the solution, mixing temperature and initial metal ions. The influence of the temperature on the ion-exchange/adsorption process was also examined. The Langmuir and Freundlich adsorption isotherm equations were derived from the basic empirical equations, and used for calculation of ion exchange parameters. Adsorption isotherms of Co^{2+} & Ni^{2+} ions could be best modelled by the Langmuir equation. The influences of contact time, metal initial concentration, adsorbent dosage concentration, and temperature have been studied. The adsorption efficiencies are found to be contact time dependent, increasing the contact time in the range of 20–180 min. The sorption equilibrium has attained between 60 and 180 min.

Keywords - Adsorption, Freundlich adsorption isotherm, ion exchange, Langmuir equation, sorption equilibrium

1. Introduction

There are different types of heavy metals which if present in excess quantities in groundwater, river water, lakes, canals, dams and other water bodies leads to serious health disorders and various diseases like irritation of the nose, mouth and eyes and it causes headaches, stomachaches, dizziness, vomiting and diarrhoea.The major sources of heavy metals in the environment include Metal Extraction, Metal Fabrication and Surface Finishing, Paint and Pigments as well as the manufacturing of batteries.

2. Zeolites

The term zeolite was originally coined in the 18th century by a Swedish mineralogist named Cronstedt who observed, upon rapidly heating a natural zeolite that the stones began to dance about as the water evaporated. Using the Greek words which mean "stone that boils," he called this material zeolite. A commonly used description of a zeolite is a crystalline aluminosilicate with a cage structure. Technically, we speak of a zeolite as a crystalline hydrated aluminosilicate whose framework structure encloses cavities (or pores) occupied by cations and water molecules, both of which have considerable freedom of movement, permitting ion exchange and reversible dehydration. This definition places it in the class of materials known as "molecular sieves." [The pores in dehydrated zeolite are 6 Ångstroms in size, while those of a typical silica gel average about 50 Å, and activated carbon averages 105 Å.] More than 150 zeolite types have been synthesized and 40 naturally occurring zeolites are known. [The formula of one of the better known zeolites is shown below.] ... Zeolites occur as hydrates, and all members of the family contain at least one silicon atom per aluminum atom.

Na-A $Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5 H_2O$
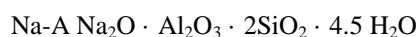
2.1 *Natural and Synthetic Formation of Zeolites*

Zeolites form in nature as a result of the chemical reaction between volcanic glass and saline water. Temperatures favoring the natural reaction range from 27°C to 55°C and the pH are typically between 9 and 10. Nature requires 50 to 50,000 years to complete the reaction. Naturally occurring zeolites are rarely phase-pure and are contaminated to varying degrees by other minerals [e.g. Fe^{++}, SO_4^-, quartz, other zeolites, and amorphous glass]. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential. Synthetic zeolites hold some key advantages over their natural analogs. The synthetics can, of course, be manufactured in a uniform, phase-pure state. It is also possible to manufacture desirable zeolite structures which do not appear in nature. Zeolite A is a well-known example. Since the principal raw materials used to manufacture zeolites are silica and alumina, which are among the most abundant mineral components on earth, the potential to supply zeolites is virtually unlimited. Finally, zeolite manufacturing processes engineered by man require significantly less time than the 50 to 50,000 years prescribed by nature. Zeolites are microporous crystalline hydrated aluminosilicates that can be considered as inorganic polymers built from an infinitely extending three-dimensional network (similar to a honeycomb) of tetrahedral TO4 units, where T is Si or Al, which form interconnected tunnels and cages. Zeolites have been widely used in heavy metals adsorption experiments due to their unique physical and chemical properties (crystallinity, thermal stability, well-defined cage structure of molecular size, ion-exchange, etc.). The advantage of zeolites over resins, apart from their much lower cost (one ton of the natural zeolite clinoptilolite costs almost €200), is their ion selectivity. Owing to zeolites structural characteristics and their adsorbent properties, they have been applied as chemical sieves, water softeners and adsorbents. Zeolites can be easily regenerated by washing them with acidic solutions (e.g. HCl) and this is one more advantage of them because they can be re-used many times without losing their adsorption capability.

2.2 *Properties of zeolites*

2.2.1. Ion exchange

Zeolites usually contain cations (e.g., Na^+, K^+, or NH_4^+) after the synthesis. These cations are required to balance the negative net-charge caused by trivalent aluminum cations which are coordinated tetrahedrally by oxygen anions. By exposing a sodium containing zeolite to a solution containing other cations, the sodium ions can be exchanged by these other cations provided they are not excluded from the pores due to their size (including the water molecules coordinating the respective cations).

2.2.2.MolecularSieveEffect/Adsorption

The pore sizes of zeolites are determined by their structures and may be varied slightly by ion-exchanging the zeolite. By this process smaller cations can be positioned in windows making them wider. Specific cations may also be positioned on other sites than in the windows, thus leading to even larger open windows. The window sizes determine the accessibility of the zeolite pore system for other (e.g. organic) molecules.

2.2.3.Acidity

As already mentioned protonated zeolites have acidic properties. The protons which balance the negative charge of a zeolite framework are not strongly bound to the framework and are able to move within the pores and react with molecules which penetrate into the zeolite pore system. A protonated zeolite thus can act as a Bronsted acid. Furthermore, Lewis acidity can be caused by cations within the pores.

2.2.4.Catalysis

Zeolites make extremely active catalysts.... Steric phenomena are very important in zeolite catalysis, and a new term, "shape selective catalysis," was coined to describe these effects. Extremely selective reactions can be made to occur over zeolites [when certain products, reactants or transition states are kept from forming within the pores because of size or shape].

3. Adsorption isotherm

The two isotherms to consider are the Freundlich and Langmuir.

3.1 *Langmuir isotherm***:** The Langmuir sorption isotherm is the best known of all isotherms describing sorption and it has been successfully applied to many sorption processes. Thus, the Langmuir isotherm model is given by the equation.

$$C_e/q_e = 1/(Q_{max}.K_L) + C_e/Q_{max} \ \dots\dots\dots\dots. (1)$$

Where,

q_e = metal concentration on zeolite at equilibrium. (mg of metal ion/g of zeolite)

Q_{max} and K_L are the Langmuir constants related to sorption capacity and sorption energy, respectively. The values of Q_{max} (mg/g) and K_L(mg–1) can be determined from the linear plot of C_e/q_e vs. C_e.

For all cases, the Langmuir model represents a better fit to the experimental data than the

Freundlich model.

Assumptions:

1 .Maximum monolayer coverage (θ=1)

2 .Energetically uniform surface.

3.No interaction between adsorbate atoms/molecules.

4 .The mechanism of adsorption does not change with surface coverage.

$r_a = Kp(1- \theta)$

$r_d = k^l \theta$

At equilibrium,

$$r_{a=} r_d$$
$$\theta = Kp/ (k^l + Kp)$$
$$= Kp/ (1 + Kp)$$
$$= v / v_m$$

Where, v= volume

v_m= corrected volume

θ = surface coverage

$(1 - \theta)$ = vacant sites

3.2. *Freundlich isotherm:*

The Freundlich isotherm, one of the most widely used mathematical descriptions, usually fits the experimental data over a wide range of concentrations. This isotherm is based on adsorption heterogeneous surfaces, the exponential distribution of active sites and their energies and adsorption enthalpy changes logarithmically.

This relation is given by:

$$\ln q_e= \ln K_F + (1/n).\ln C_e\dots\dots\dots\dots\dots\dots(2)$$

where,

qe = the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg/g),

Ce is the equilibrium concentration in mg/l,

K_F = roughly an indicator of the adsorption capacity (mg/g)

1/n = a characteristic constant for the adsorption system (g/L).

K_F and n can be determined from the graph between $\ln q_e$ vs $\ln C_e$.

K_F = slope and n = intercept.

4. Conclusion

In the present study, appopolite, natural zeolite has been successfully used for removal of Co and Ni ions from the aqueous model solution. The maximum adsorption of Co has been found at the dosage 5g/l.

In between cobalt and nickel cobalt exhibited a higher percentage removal. In addition to this:

1. Adsorption of lead, cobalt, and nickel onto appopolite (natural zeolite) has an ion-exchange nature. Three different stages are observed in the ion exchange adsorption of the metals. The process begins with fast adsorption on the appopolite micro crystal surface during the first 20 minutes. Nearly 80% of Copper and 75% of nickel adsorbed during the first stage on the micro crystals surface.

2. The ion exchange of metals is directly proportional to pH value of aqueous solutions. Adsorbtion decreases in the more acidic medium.

3. The slight difference between adsorption capacity of the appopolite towards Copper and Cadmium from single and multicomponent solutions may testify to individual sorption centres of the zeolite for each of these metals.

4. Efficiency of metals removal from solutions by appopolite is inversely proportional to the metal concentration. The metals from the following order for adsorption efficiency: $Pb^{2+} > Cu^{2+} > Cd^{2+} > CO > Ni^{2+}$.

5. The data obtained from the studies are applied well to the Langmuir isotherm in comparison to the Freundlich isotherm.

References

Hiraoki katusuki et.al, "Rapid synthesis of Monodispersed α- Fe2O3 Nanoparticles from Fe(NO3)3 solution by microwave irradiation",Journel of the ceramics society of Japan ,112[7]384-387(2004)

J.Salado et.al, "Synthesis and magnetic properties of monodispersed Fe2O3 nanoparticles with controlled sizes",Journal of Non-crystalline solids ,354(2008),5207-5209

Brianna R White et.al, "Magnetic ɤ - Fe2O3 nanoparticles coated with poly-L-cysteine for chelation of As(III), Cu(II), Cd(II), Ni(II), Pb(II), and Zn(II)",Journal of hazardous materials,161(2009),848-853

Soamwadee chaianansutcharit et.al, "Synthesis of Fe2O3 nanoparticles in different r,eaction media"Ceramics International ,33(2007),697-699

Jie chen et.al, "Preparation of Fe3O4 nanoparticles with adjustable morphology",Journal of alloys and compounds,(2008) ,Article in press.

I.G.Parsons et.al., "Determination of arsenic(III) and arsenic(V) binding to microwave assisted hydrothermal synthetically prepared Fe3O4,Mn3O4 and MnFe2O4 nanoadsorbents",Microchemical Journal, 91(2009),100-106.

Zhong Jie Zhang et.al, "Hydrothermal synthesis and self assembly of magnetite(Fe3O4) nanoparticles with the magnetic and electrochemical properties", Journal of crystal growth 310(2008),5453-5457.
Pratap Chutia et.al, "Adsorption of As(V) on surfactant modified natural zeolites"Journal of Hazardous materials,162(2009),204-211

Yu-Ting Zhou et.al, "Removal of Cu2+ from aquous solution by chitosan-coated magnetic nanoparticles modified with -ketoglutaric acid", Journal of colloid and interface science, 330(2009),29-37.

Panagiota Stathi et.al, "Physicochemical study of novel organoclays as heavy metal ion adsorbents for environmental remediation",Journal of colloid and interface science, 316(2007),298-309

Comparison &interpretation of adsorption isotherms

Table 1: Isotherm data for Nickel(Ni):

C_O(ppm)	Ce(ppm)	q_e= c_o-c_e	Ln ce	Ln qe	Ce/ qe	time
100	69.23	30.77	4.23743429	3.42654019	2.24992	20
100	48.42	51.58	3.87991295	3.943134	0.93874	60
100	48.14	51.86	3.87411343	3.94854778	0.92827	120
100	47.8	52.2	3.86702564	3.95508249	0.91571	180
300	120	180	4.78749174	5.19295685	0.66667	20
300	100.8	199.2	4.61313836	5.29430935	0.50602	60
300	89.25	210.75	4.49144142	5.3506726	0.42349	120
300	85.4	214.6	4.4473461	5.36877583	0.39795	180
500	194.7	305.3	5.27145991	5.7212949	0.63773	20
500	166.89	333.11	5.11733491	5.80847277	0.50101	60
500	173	327	5.15329159	5.78996017	0.52905	120
500	150.2	349.8	5.01196774	5.85736156	0.42939	180

Table 2: Isotherm data for Cobalt(Co):

CO(ppm)	Ce(ppm)	qe= co-ce	Ln ce	Ln qe	Ce/ qe	time
100	31.06	68.94	3.43592082	4.23323656	0.4505367	20
100	28.056	71.944	3.33420251	4.27588804	0.38996998	60
100	27.763	72.237	3.3237042	4.27995238	0.38433213	120
100	25.17	74.83	3.22565281	4.31521887	0.33636242	180
300	55.357	244.643	4.01380312	5.49980001	0.22627666	20
300	52.49	247.51	3.96062268	5.51145099	0.21207224	60
300	48.49	251.51	3.88135759	5.52748275	0.19279552	120
300	45.23	254.77	3.81176058	5.54036118	0.17753268	180
500	94.81	405.19	4.55187489	6.00435609	0.23398899	20
500	89.63	410.37	4.49569009	6.01705919	0.21841265	60
500	82.21	417.79	4.40927695	6.03497891	0.1967735	120
500	81.85	418.15	4.4048883	6.03584022	0.19574315	180