ISSN 2231-3478 (Print)

JUSPS-B Vol. 34(2), 6-15 (2022). Periodicity-Monthly

Section B

(Online) ISSN 2319-8052

JOURNAL OF ULTRA SCIENTIST OF PHYSICAL SCIENCES

An International Open Free Access Peer Reviewed Research Journal of Physical Sciences

website:- www.ultrascientist.org

Estd. 1989

Removal of heavy metals (Nickel and Molybdenum) from wastewater using low cost adsorbents (China clay and Fly ash)

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http://dx.doi.org/10.22147/jusps-B/340201

Acceptance Date 01st February, 2022, Online Publication Date 27th February, 2022

Abstract

The present paper reveals that the potential of China clay and Fly ash were used as adsorbent for the removal of heavy metals such as Ni(II) and Mo(VI) from known concentration of waste water was investigated. Hence the study indicates that the low cost adsorbent of China clay is used for removing 90% and 69% of Ni(II) and Mo(VI) respectively. Fly ash used for removing 84% and 77.6% of Ni(II) and Mo(VI) from wastewater from the initial metal ion concentration of $4.26x10^{-5}$ M and $1.49x10^{-5}$M solution respectively. Batch adsorption studies demonstrated that the adsorbents had significant capacity to adsorb Ni(II) and Mo(VI) from aqueous solution. It was found that the adsorption increased with increase in contact time. Also, percentage adsorption depends on change in pH of N(II) and Mo(VI) solution.

Key words : Heavy metals, Adsorbents, Effect of Contact time and Agricultural waste.

Introduction

Mineral adsorbents such as zeolite, silica, and clay are considered good candidates for water purification with low operating costs[1]. Clay has extraordinary cation exchange capacity, cation exchange selectivity, surface hydrophilicity, high swelling/expanding capacity, and surface electronegativity[2]. In addition, acid washing, thermal treatment, and pillar bearing could enlarge the pore size, pore volume, and specific surface area, leading to a remarkable increase in the adsorption efficiency[2]. Research studies showed that physical adsorption, chemical adsorption, and ion exchange are the most common mechanisms controlling wastewater treatment using mineral adsorbents. Besides the mentioned parameters, the pH, temperature, adsorption time, and adsorbent dosage are also considered vital parameters controlling the adsorption process.

The presence of toxic heavy metals such as Ni(II) and Mo(VI) contaminants in aqueous streams, arising from the discharge of untreated metal containing effluents into water bodies, is one of the most important environmental problems. Environmental pollution is currently one of the most important issues facing humanity. It was increased exponentially in the past few years and reached alarming levels in terms of its effects on living creatures. Toxic heavy metals are considered one of the pollutants that have direct effect on man and animals[5]. Inputs of these trace metals into ecosystem are largely as a result of mining operations, refining ores, sludge disposal, fly ash from incinerators, processing of radioactive materials, metal plating, or manufacture of electrical equipment, paints, alloys, batteries, pesticides and preservatives[6]. The discharge of metallic ions in industrial effluent is of great concern because their presence and accumulation have a toxic effect on living species [7].

Materials and Methods

1: Adsorbents and their Characterization :

The physico-chemical nature of the adsorbates significantly affects the rate and extent of adsorption of pollutants from water and wastewaters by adsorption technique. The chemical constituents of various adsorbents vary from sample to sample depending upon the source of collection. Therefore, the characterization of adsorbents is quite essential in order to have a better insight into the mechanism of the adsorption process. The surface charges of the adsorbent can be enhanced by surface functional groups to improve the heavy metal uptake[3]. China clay is a mineral of kaolinite group. It does not swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers [Nordell, 1961., Boyd et al., 1947., Eliassen, et al., 1965, Lefevie. 1986., Mantell, 1951.,] as an adsorbent for water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur district, Bihar (India). It was used as such without any pretreatment just after sieving through 53µm pore size sieve. The different chemical constituents of adsorbents were determined using gravimetric, EDTA and colorimetric methods [Indian Standard Methods, 1960., Roy et al 1965.,]. The chemical analysis and characterization of China clay is given in Table 1.

Fly ash was obtained from Obera Thermal Power Plant, Mirzapur, UP (INDIA). They were used as such without any pretreatment just after sieving through 53µm pore size sieve (Table:2).

Table 1: Chemical analysis of China clay as Adsorbent

Constituents	Percentage by weight
SiO_2	46.22
Al_2O_3	38.40
CaO	0.86
Fe_2O_3	0.68
MgO	0.37
Loss of ignition	13.47
Particle size	53µm
Mean Particle size diameter	51×10^{-4} cm
Surface Area	13.52 $m^2 g^{-1}$
Porosity	0.330
Density	2.692 gcm^{-3}

2: Batch adsorption studies :

Table 2: Chemical analysis of Fly ash as Adsorbent.

Constituents	Percentage by weight
SiO_2	56.04
$Al_2 O_3$	25.90
CaO	2.22
Fe_2O_3	1.26
MgO	0.94
Loss of ignition	13.64
Particle size	53µm
Mean Particle size diameter	$48x10^{-4}$ cm
Surface Area	5.77 m^2g^{-1}
Porosity	0.360
Density	3.420 gcm^{-3}

The metal solutions used in this study were prepared as the stock solutions. 100ml of adsorbate solution of known concentration was taken in the 250 ml conical flask and 1gm of each adsorbent was added separately at definite pH and temperature. For a wide range contact time 20 - 180minutes. After that the solution was filtered by whatmann 42 filter paper and concentration of the filtered solution was determined by atomic absorption spectrophotometer[8]. The percentage removal was determined by the following expression. The amount of adsorption efficiency was calculated by,

$$\text{Percentage adsorption} = \left[\frac{Co - Ce}{Co}\right] x100$$

Where, Co = initial concentration of metal ion in the solution and Ce = final concentration of metal ion in the solution.

3: Effect of Contact Time on Adsorption of Heavy Metals :

The percentage of adsorption is found to increase continually with time till the equilibrium is attained with saturation at 180 minutes. The percentage adsorption of Ni(II) is 55-93 and 30-80 for China clay and fly ash respectively. This may be due to utilization of active sites is larger surface area[6]. Then percentage reduction of Mo(VI) is 30.61-73.47 and 20.4- 68.16 for China clay and Fly ash respectively. The decreased adsorption efficiency is due to less adequate availability of active sites on the adsorbents [Boud et al 1947.,] (figure: 1). The high percentage reduction of Ni(II) and Mo(VI) is found to be 93 and 73.47 for China clay adsorbent is rapidly decreased. It has been observed that the percentage of Ni(II) adsorption increased with increasing agitation speed due to the proper contact between the metal ions in solution and the adsorbents binding sites that promotes effective transfer of Ni(II) ions to the adsorbents sites[9]. This increase maybe due to the activation of adsorption site takes place leading to increased adsorption probably through surface exchange mechanism[10]. This may be due to the smaller size of adsorbent in the metal solution provided a greater availability of the metal ions to penetrate to the internal pore structure of the adsorbent. The lower metal uptake with larger adsorbent particles was due to the high diffusion resistance to mass transport[11].

Table 3: Effect of Contact Time on Adsorption of Ni(II) at different contact time, At Temperature 30°C, pH 6.5 and concentration 4.26×10^{-5}M. China clay as Adsorbent

Time(min)	Amount adsorbed (mg g^{-1})	% Adsorption
20	0.0300	24.00
40	0.0400	32.00
60	0.0625	50.00
80	0.0750	60.00
100	0.0950	76.00
120	0.1025	82.00
140	0.1075	86.00
160	0.1100	88.00
180	0.1125	90.00
200	0.1125	90.00

Table 4: Effect of Contact Time on Adsorption of Ni(II) at different contact time, At Temperature 30°C, pH 6.5 and concentration 4.26×10^{-5}M. Fly ash as Adsorbent.

Time(min)	Amount adsorbed(mgg^{-1})	% Adsorption
20	0.0175	14.00
40	0.0300	24.00
60	0.0550	44.00
80	0.0700	56.00
100	0.0900	72.00
120	0.0950	76.00
140	0.1000	80.00
160	0.1025	82.00
180	0.1050	84.00
200	0.1050	84.00

Table 5: Effect of Contact Time on Adsorption of Mo(VI) at different contact time, At Temperature 30°C, pH 6.0 and concentration 1.49×10^{-5}M. China clay as Adsorbent.

Time(min)	Amount adsorbed(mg g^{-1})	% Adsorption
20	0.026530	26.53
40	0.040817	40.81
60	0.055102	55.10
80	0.061350	61.35
100	0.067342	67.34
120	0.070320	70.32
140	0.077563	77.56
160	0.080408	80.40
180	0.081633	81.63
200	0.081833	81.63

Table 6: Effect of Contact Time on Adsorption of Mo(VI) at different contact time, At Temperature 30°C, pH 6.0 and concentration $1.49x10^{-5}$M. Fly ash as Adsorbent.

Time(min)	Amount adsorbed(mg g-1)	% Adsorption
20	0.014286	14.28
40	0.026252	26.25
60	0.032153	32.15
80	0.045306	45.30
100	0.055918	55.91
120	0.068163	68.16
140	0.073872	73.87
160	0.075852	75.85
180	0.077551	77.55
200	0.077551	77.55

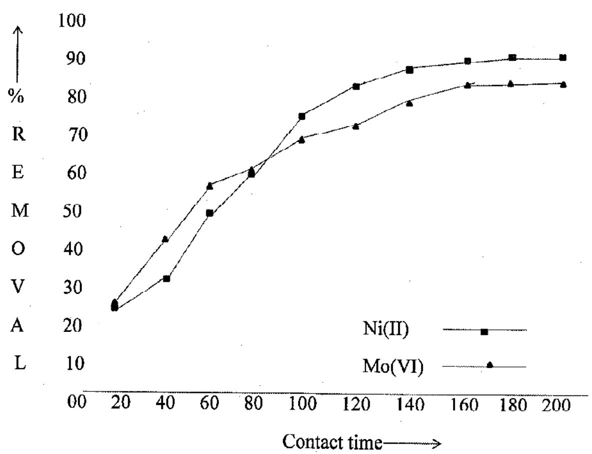


Figure 1. Percentage removal of Ni(II) and Mo(VI) from China clay.

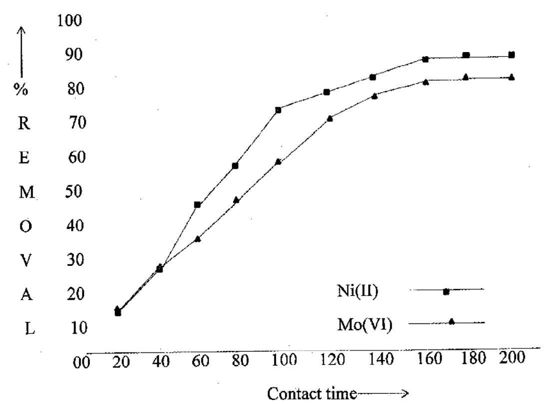


Figure 2. Percentage removal of Ni(II) and Mo(VI) from Fly ash.

4: Effect of pH on Adsorption of Heavy Metals :

The removal of Ni(II) and Mo(VI) from water and wastewater by adsorption on China clay and Fly ash were mainly influenced by the pH of the system. It affects the surface charge of the adsorbent, degree of ionization and speciation of aqueous metal ion solutions. Three types of mechanism were suggested by Mac-Naughton and James for heavy metals removal from aqueous solutions.

(i) Ion exchange reactions.

(ii) Metal ion adsorption at hydrated oxides of the surface.

(iii) Metal hydroxyl species adsorption at hydrated oxide surface.

The effect of pH on adsorption of Ni(II) on China clay and Fly ash was studied at pH 3.0, 4.0, 5,0, 6.5, 7.0, 8,0 and 9.0. The maximum adsorption capacity of both the adsorbents was found to be at pH 7.0.0 in case of Ni(II) and at pH 6.0 in case of Mo(VI) (Figure:3). The saturation time in each system remains unaltered with the change in pH value of adsorbate solution. The percentage removal of Ni(II) on China clay and Fly ash increases from 50 – 95 and 45 – 90 with increase in pH 4.0 – 7.0 respectively and thereafter it starts decreasing from 95 – 80 for China clay and 90 – 62 for Fly ash from increase of pH from 7.0 to 8.0. Similarly, The percentage removal of Mo(VI) on China clay and Fly ash increases from 44.08 – 81.63 and 34.69 – 77.55 with increase in pH 4.0 – 6.0 respectively and thereafter it starts decreasing from 81.63 – 20.81 for China clay and 77.55 – 10.20 for Fly ash from increase of pH from 6.0 to 8.0.. It was observed that Maximum percentage adsorption occurs at pH 7.0 in case of Ni(II) and at pH 6.0 in case of Mo(VI).

The variation of percentage adsorption with the change in pH of the adsorbate solution in each system has also been presented graphically (figure:3). The adsorption removal efficiency increases when the pH increases and the initial concentration decreases[4]. The rate and extent of adsorption of metal cations on various adsorbent may be explained on the basis of surface hydroxylation of oxides present in the adsorbent s at the solid-solution interface and its subsequent acid-base dissociation which makes the surface positively or, negatively charged depending on the variation of pH of the medium. The change in the surface charge occurs in the following manner[15-19].

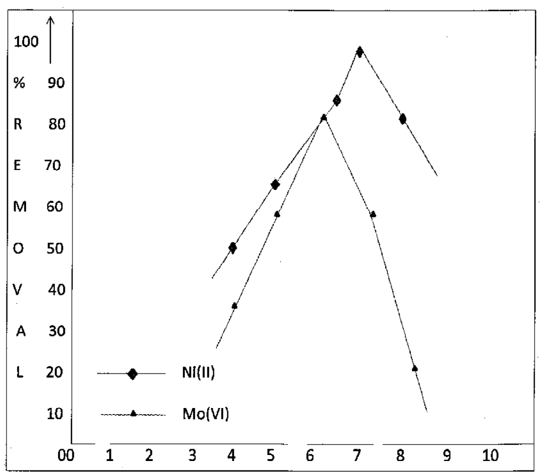


Figure-3: Effect of pH on adsorption of Ni(II) and Mo(VI) on China clay.

Table 7. Effect of pH on Adsorption of Ni(II) at temperature 30°C and concentration 4.26×10^{-5}M. China clay as Adsorbent

Time(min)	Amount adsorbed(mg g^{-1})	% Adsorption
4.0	0.1250	50.00
5.0	0.1600	64.00
6.5	0.2125	85.00
7.0	0.2375	95.00
8.0	0.2000	80.00

Table 8. Effect of pH on Adsorption of Ni(II) at temperature 30ºC and concentration $4.26x10^{-5}$M. Fly ash as Adsorbent.

Time(min)	Amount adsorbed(mgg^{-1})	% Adsorption
4.0	0.1125	45.00
5.0	0.1450	58.00
6.5	0.1750	70.00
7.0	0.2250	90.00
8.0	0.1550	62.00

Table 9. Effect of pH on Adsorption of Mo(VI) at temperature 30ºC and concentration $1.49x10^{-5}$M. China clay as Adsorbent

Time(min)	Amount adsorbed(mg g^{-1})	% Adsorption
4.0	0.044082	44.08
5.0	0.060000	60.00
6.0	0.081633	81.63
7.0	0.053143	57.14
8.0	0.020816	20.81

Table 10. Effect of pH on Adsorption of Mo(VI) at temperature 30ºC and concentration $1.49x10^{-5}$M. Fly ash as Adsorbent

Time(min)	Amount adsorbed(mg g^{-5})	% Adsorption
4.0	0.034694	34.69
5.0	0.052245	52.24
6.0	0.077551	77.55
7.0	0.044898	44.89
8.0	0.010204	10.91

Where, M stands for Al, Si, Fe, Ca, Mg etc. It is clear from above eqilibria that the positive charge density on the surface of the adsorbent increases with the decrease in the pH of the solution and hence, adsorption of cations decreases. At high pH, the surface is more negatively charged which favors the removal of cations. Maximum removal of Ni(II) at pH 7.0 was also noted by Radi Salim.Similarly, Maximum removal of Mo(VI) at pH 6.0 was noted by Radi Salim.

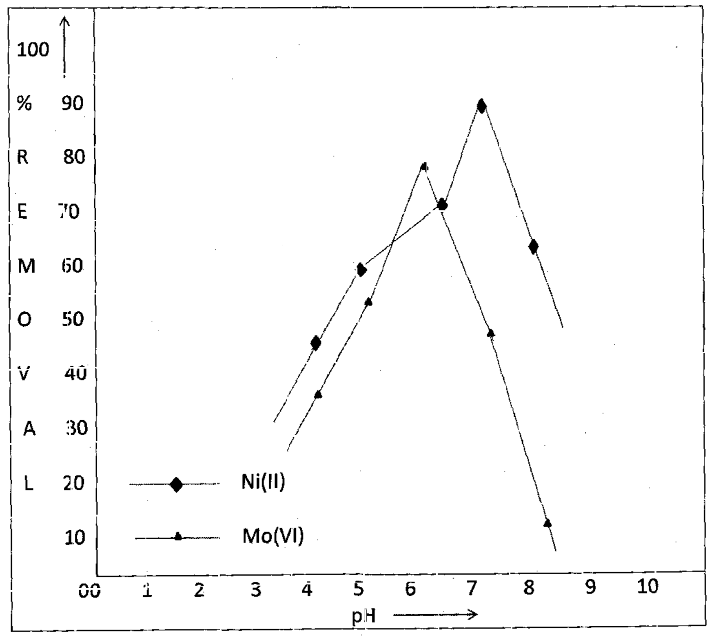
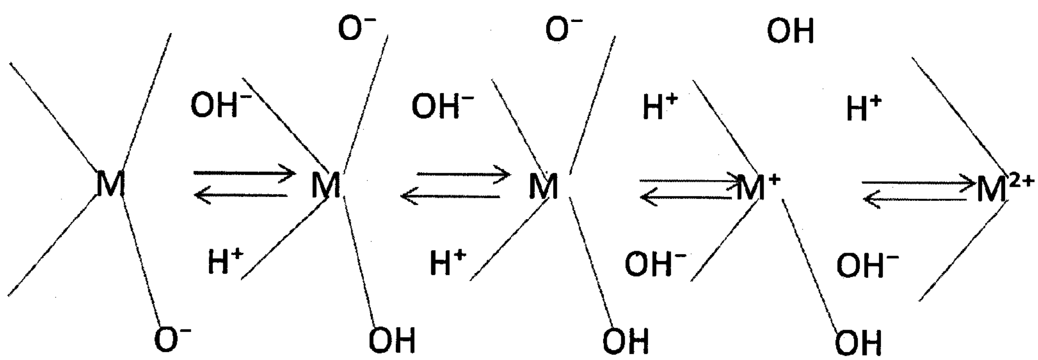


Figure-4: Effect of pH on adsorption of Ni(II) and Mo(VI) on Fly ash.



Conclusion

In the present study heavy metals such as nickel and molybdenum were selected for removal from aqueous solutions using adsorption technique. A particle size of 53 µm was observed to be highly efficient for the nickel and molybdenum. This work showed that the various adsorbents could be used as a good adsorbent material for nickel and molybdenum for wastewater treatment. The present adsorbents (China clay and Fly ash) can be used as an industrial scale to remove the nickel and molybdenum respectively. Hence, it is necessary to remove these metals from industrial effluents before discharging waste water into the environment.

SCOPE OF FUTURE WORK

Among all methods, adsorption is the most considered method in recent years. It showed easy operation, low-cost, and high sorption capacity. Developing eco-friendly and cost-effective adsorbents from wastes is the current research trend. However, disposal of such adsorbents after the adsorption process is a big challenge to avoid environmental risks. Adsorption onto adsorbents was reported as a feasible method for industrial scale. Adsorption of metal ions from low traces and efficient regeneration processes need additional research. The economic feasibility of industrial applications is also essential. Selection of the most appropriate technique for heavy ions removal from wastewater depends on many key factors, including the operation cost, initial concentration of the metal ions, environmental impact, pH values, chemicals added, removal efficiency, and economic feasibility. These methods are classified as adsorption treatments using different adsorbents. Adsorption is the most promising method widely investigated in removing heavy metal ions from wastewater due to simple operation, strong applicability, high removal rate, and low cost of reusability. However, this preference depends mainly on selecting low-cost materials, high uptake, and efficient regeneration processes. In general, adsorption method is the most practical method addressed in the literature. It has been noticed that this is one of the best method for the removal of heavy metal ions from real Wastewater. Accordingly, additional research should be conducted using real wastewater for treating different contaminants. More research on introducing cost effective materials and methods for heavy metal removal from wastewater should be carried out. Future studies should also focus on the pilot-scale process. The best techniques to achieve efficient metals recovery with less environmental impact and low cost are still under development and should be considered in future research.

Acknowledgement

I take this opportunity to express my deep sense of gratitude and indebtedness to Dr C P Singh (Retd Principal and Head) and Dr Anil Kumar (Associate Prof) Department of Chemistry, Sahu Jain P G College Najibabad , Distt- Bijnour (UP) INDIA, for suggesting the research problem, excellent guidance, valuable suggestions, constant encouragement and financial support throughout the present investigations.

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