

Adsorption Study of Heavy Metals Removal from Wastewater Using PVA- Nano Ferrite Composites

V. Manimozhi¹, R. Saravanathamizhan^{1,*}, E. KT. Sivakumar² and V. Jaisankar³

¹Department of Chemical Engineering, A.C.Tech Campus, Anna University, Chennai-600025, India.

²Department of Ceramic Technology, A.C.Tech Campus, Anna University, Chennai- 600025, India.

³PG and Research Department of Chemistry, Presidency College (Autonomous), Chennai-60000, India.

(*) Corresponding author: thamizhan79@rediffmail.com
(Received: 29 August 2019 and Accepted: 15 January 2020)

Abstract

The aim of the present investigation is to synthesize Barium ferrite and Nickel ferrite Nanoparticles by co-precipitation method and these nanoparticles are used to prepare nanocomposites with poly vinyl alcohol (PVA). The composited nanoparticles are characterized by using FTIR, XRD and SEM. The synthesized nanoparticles are used as adsorbent to remove the heavy metals such as Cu^{2+} , Cd^{2+} , Pb^{2+} from simulated industrial waste water. The experimental parameters such as contact time, adsorbent dosage and pH have been studied on the percentage removal of metal ions. It is observed from the experiment, that 100% and 99.05% of Cu^{2+} has been removed by PVA-Barium and PVA-Nickel ferrite nanocomposites respectively. The experimental data were analyzed using the Langmuir and Freundlich isotherm. The synthesized nanoparticles have greater potential for adsorption of heavy metal ions present in simulated industrial wastewater. These nanoparticles with polymeric composites can be effectively used as adsorbents in the commercial scale to achieve the desired goal of clean environment.

Keywords: Ferrite nanoparticles, Metal ions, Adsorption, Poly Vinyl Alcohol-nanocomposites.

1. INTRODUCTION

The presence of heavy metals ions such as copper, iron, nickel, lead, etc., in the environment are of major concern due to their toxicity to many life forms [1-3]. The tremendous increase in the use of these heavy metals over the past few years resulted in an increased flux of metallic substances in the environment. The industrial waste constitutes the major source of various kinds of metal pollution in natural water. The important toxic metals from these sources are cadmium, copper, lead, nickel and arsenic [4]. These toxic heavy metals entered into the water bodies through waste water from metal plating industries [5] and industries of Ni-Cd batteries [6], phosphate fertilizer [7], mining [8], pigments [9] and stabilizers

alloys [10]. The effect of metal poisoning in humans are serious, it induces and creates high blood pressure, kidney damage and destruction of red blood corpuscles. Unlike organic pollutants, which are susceptible to biological degradation, metal ions do not degrade into any harmless end products and tend to accumulate in living organisms, causing various diseases and disorders [11, 12].

There are various technologies that have been developed over the years, the most important includes chemical precipitations, electro floatation, ion exchange, reverse osmosis and adsorption [13-16]. Most of these methods suffer from some drawbacks such as high capital, operation cost and the disposal of the residual metal sludge which

are not suitable for small scale industries. Considering limitations of conventional methods for metal removal, the most promising alternative method appears to be the adsorption method. The adsorption method is exclusively used for the water treatment and the process is mainly physico-chemically-feasible process. Also, this method is a user friendly, cost effective process for the removal of metallic micro pollutants from water. The adsorption technique is superior to other techniques for reuse in terms of the initial cost, simplicity of design, ease of operation and insensibility to toxic substances [17-21].

Nanomaterials have a wide range of applications, as in the technological and environmental challenges in the areas of solar energy conversion, catalysis, medicine, and water treatments. There are several studies which have addressed that nanoparticle, especially, metal oxide nanoparticles are effective and efficient adsorbents in the cleanup of environmental contaminants. In this context, ferrites nanoparticles paved way to a new and exciting research field, with revolutionary applications not only in the electronic technology but also in the field of environmental remediation.

Alqadami et al [22] synthesized novel nanocomposites ($\text{Fe}_3\text{O}_4@\text{TAS}$) for the removal of Cd(II), Cr(III) and Co(II) from aqueous solution. The author reported the maximum adsorption capacities of adsorbent for the metal removal of Cd(II), Cr(III) and Co(II) is 286, 370 and 270 mg/g respectively. The research group of Alqadami et al [23] developed a magnetite-based metal – organic frame ($\text{Fe}_3\text{O}_4@\text{AMCA-MIL53 (Al)}$) for the removal of U(VI) and Th(IV) metal ions from aqueous solution. They reported that the adsorption capacity was 227.3 and 285.7 mg/g for U(VI) and Th(IV), respectively. Shahat et al [24] prepared nano adsorbent for the removal of Pb(II) ions from aqueous solutions. The author reported that sorption capacity was 169.34

mg/g. Mironyuk et al [25] synthesized mesoporous carbonated TiO_2 nanoparticles and it is used as an adsorbent for Sr(II) removal from aqueous medium. The authors reported that adsorption capacities of modified 2C- TiO_2 , 4C- TiO_2 and 8C- TiO_2 samples were 170.4, 204.4, 190.8 mg/g respectively, while it was 70.9 mg/g for the unmodified TiO_2 towards Sr(II). In this view, adsorbent is prepared with polymer material to form composites.

A polymer composite is a composite material composed of a variety of short or continuous fibers bound together by an organic polymer matrix. Polymer composite are designed to transfer loads between fibers through the matrix. Some of the advantages of polymer composite include their lightweight, high stiffness and their high strength along the direction of their reinforcements. Other advantages are good abrasion resistance and good corrosion resistance. In general polymethacrylate, poly vinyl acetate and poly acrylic acid can be used for immobilization of nanoparticles. Polyvinyl alcohol is a polymeric material containing large number of hydroxyl groups. PVA has been widely applied because it has many advantages such as low cost, non-toxicity, high durability and chemical stability. Further it is reported that PVA based materials shows a good removal of heavy metals from aqueous solutions.

The present investigation, nanoparticles are synthesized by co-precipitation method and composites are prepared using PVA. The composited nanoparticles are characterized by using FTIR, XRD and SEM. The synthesized nanoparticles were used as adsorbent to remove the heavy metals such as Cu^{2+} , Cd^{2+} , Pb^{2+} from simulated industrial waste water. The influences of the factors such as contact time, adsorbent dosage and pH have also been studied.

2. EXPERIMENTAL

2.1 Materials

The materials used for the synthesis of barium ferrite and nickel ferrite nanoparticles were ferric chloride, nickel chloride, barium chloride and sodium hydroxide, PVA purchased from Merck, were of purity 98-99%.

2.2 Synthesis of Barium and Nickel Ferrite Nanoparticles

The barium ferrite and nickel ferrite nanoparticles were prepared by simple and inexpensive co-precipitation method [26]. The starting materials, Barium chloride and Iron chloride hexahydrate are taken in 1:2 mol ratios, in aqueous medium. Barium chloride solution and Iron chloride solution were mixed and alkalisied using strong alkali of 1.5 M NaOH solution adding drop by drop with constant stirring using magnetic stirrer to adjust the pH of solution to 7. The solution was then brought to reaction temperature about 80°C and stirred for two hours. After stirring, the solution was cooled and washed by repeated decantation with water, till it is free from chloride ions. The product obtained were centrifuged for 20 minutes and dried overnight at 100°C. The Nickel ferrite nanoparticles were prepared by the above method using nickel chloride instead of barium chloride and iron chloride.

2.3 Polyvinyl Alcohol and Nickel Ferrite and Barium Ferrite Composite

Initially PVA (1g) was dissolved in 25 ml of water on heating, after complete dissolution, 2.5 gm of barium ferrite nanoparticles was added to it. Then it was dispersed using magnetic stirrer for 3 hours at 50°C. The solution was poured into petri dish and the solvent was evaporated at 50°C overnight, to cast into film. The obtained film was stored in the desiccators to keep out from moisture. The PVA nickel nano ferrite nanocomposites were prepared by using the nickel nano ferrite in the above method instead of barium ferrite nanoparticle.

2.4 Characterization of Nanoparticles

Synthesized barium and nickel ferrite nanoparticles were characterized by spectral analysis and thermal analysis. Fourier- Transform Infrared (FTIR) spectroscopy, IR Spectra of the PVA-barium and PVA-nickel ferrite nanocomposites were recorded using a Perkin Elmer IR spectrometer in the range of 4000cm⁻¹ to 400cm⁻¹. The X-ray diffraction (XRD) patterns of the barium and nickel ferrite nanoparticles were obtained with CuK α (λ = 0.1542 nm) radiation on a D8 Advance (Bruker-AXS) diffractometer. The XRD patterns were recorded in the 2 θ range of 20–60° and were utilized for quantitative phase analysis. The mean crystallite size (D) of the particle was calculated from the XRD line-broadening measurement from the Scherrer equation. The structure and morphology of the PVA-barium and PVA-nickel ferrite nanocomposites were studied using a HITACHI S2600N-type scanning electron microscope (SEM). The compositional analysis of the above composites were carried out by EDAX analysis using a JEOL GSM-5900 scanning electron microscope.

2.5 Batch Adsorption Study

The adsorption of heavy metals on adsorbent was studied by batch experiment. A known weight of adsorbent (e.g. 0.1g adsorbent) was equilibrated with 25 ml of the heavy metal namely Pb²⁺, Cd²⁺, Cu²⁺ solution of known concentration (5, 10, 20 mg/L) in three stoppered brosil glass flask at 25°C for a known period (30–150 min.) of time. In the regular intervals of 30,60,90,120 and 150 minutes, 10 ml of sample was collected from each flask and the suspension of the adsorbent was separated from solution by filtration using Whatman No. 1 filter paper. The concentration of heavy metal ions remaining in solution was measured by Atomic Absorption Spectrophotometer. The effect of several parameters, such as pH, concentrations,

contact time and adsorbent dose on the metal ion removal were studied. The amount of metal ions adsorbed by the adsorbent was evaluated using equation (1):

$$q_t = \frac{(C_0 - C_t)v}{w} \quad (1)$$

The mass balance equation was used to determine the adsorption capacity (q_e) from equation (2):

$$q_e = \frac{(C_0 - C_e)v}{w} \quad (2)$$

The percentage of metal ions removed was obtained from equation (3):

$$R(\%) = \frac{(C_0 - C_t) \times 100}{C_0} \quad (3)$$

where, C_0 and C_t are the initial and final concentrations of the heavy metals present in wastewater before and after adsorption, for a period of time t (mg/L) respectively; C_e represent the concentrations of heavy metals in wastewater (mg/L) when equilibrium was attained; the volume of wastewater used is represented by v (liter); w represent the mass (g) of the adsorbent used.

3. RESULT AND DISCUSSION

3.1 Scanning Electron Microscopy for PVA –Ferrite Nanocomposites

SEM images of PVA-barium ferrite and PVA-nickel ferrite nanocomposites are shown in Fig. 1(a) & 1(b) respectively. It reveals that the sample exhibit a compact arrangement of homogeneous nanoparticles with spherical in shape. It has been observed that the particles are not agglomerated, having almost uniform size distribution and the average size of PVA-barium ferrite nanocomposites ranges from 66.5 nm to 105 nm. PVA-Nickel ferrite nanocomposites size ranges from 44.nm to 66.7 nm .The values are in good agreement with the value calculated using XRD method.

3.2 EDAX Analysis

Energy dispersive X-ray spectroscopy (EDS, EDX or EDXRF) is an analytical technique used for the elemental analysis or chemical characterization of a sample.

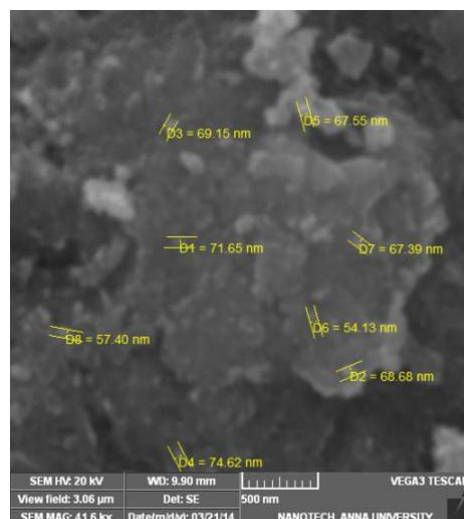


Figure 1 (a). SEM Image PVA- barium ferrite nanocomposites.

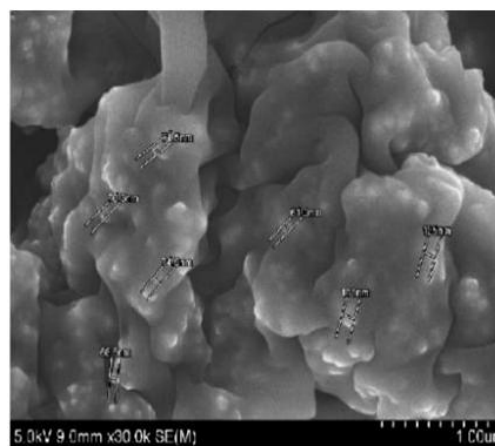


Figure 1 (b). SEM Image PVA- nickel ferrite nanocomposites.

As a type of spectroscopy, it relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. To stimulate the emission of characteristic X-rays from a specimen, a high energy beam of charged particles such as electrons or a beam of X-rays, is focused onto the sample that is being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole. An electron from an outer, higher-energy

shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of X-rays. The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured. The compositional analysis of the PVA-barium ferrite and PVA-nickel ferrite nanocomposites were carried out by EDAX analysis using a JEOL GSM-5900 scanning electron microscope. The EDAX spectrum is shown in Figure 2(a)&2(b). Peak corresponding to barium, nickel, carbon, iron, oxygen were found in the spectrum.

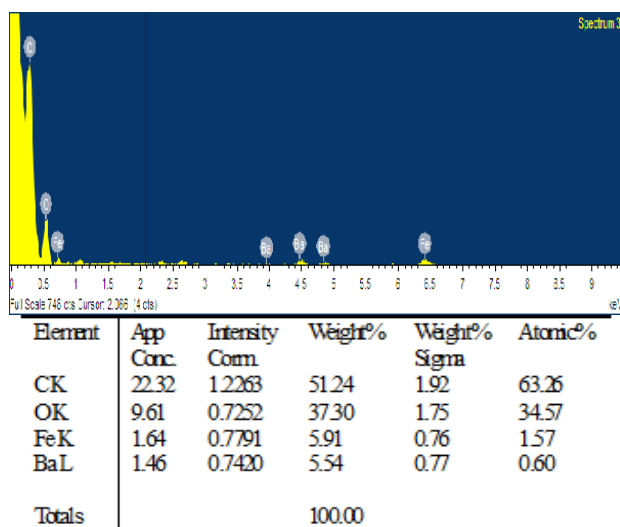


Figure 2 (a). EDX image and composition of PVA-barium ferrite nanocomposites

3.3 Fourier-Transform Infrared (FT-IR) Spectroscopy

IR spectroscopy is the most extensively used tool for the analysis of functional groups. This technique is based upon the simple fact that a chemical substance shows marked selective absorption in the infrared region giving rise to close-packed absorption bands called an IR absorption spectrum, over a wide wavelength range.

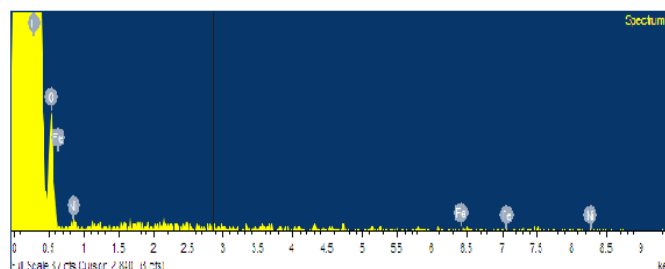


Figure 2 (b). EDX Image and composition of PVA-nickel ferrite nanocomposites.

Thus, an IR spectrum of a chemical substance is a fingerprint for its identification. The FT-IR spectra recorded for the PVA-barium ferrite and PVA-nickel ferrite nanocomposites are shown in Figure 3(a) and 3(b). The band appears at 3500 cm^{-1} is assigned for the stretching vibrations of $-\text{OH}$ groups. The band at $1798\text{--}1418\text{ cm}^{-1}$ indicates flexible vibrations of $-\text{OH}$ groups. The peaks around 2939 cm^{-1} and at 1450 cm^{-1} correspond to the $\text{C}-\text{H}$ stretching and $-\text{CH}_2-$ bending from alkyl groups, respectively. At low wave number, the band in the range of $800\text{ to }664\text{ cm}^{-1}$ corresponds to metal-oxygen ($\text{Fe}-\text{O}$) stretching vibrations and it is characteristic band of PVA-barium ferrite and PVA-nickel ferrite nanocomposites peak is observed as shown in the figure 3a and 3b.

3.4 XRD Analysis

The X-ray diffraction patterns of the synthesized nickel and barium PVA-composites are shown in Figure 4(a) and 4(b), which indicates the presence of the spinel cubic structure.

The average crystalline diameter (D) was calculated by Scherrer's equation. The average crystalline sizes of barium and nickel ferrite nanoparticle were calculated as 90nm and 75nm respectively.

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (4)$$

where, β is the line broadening at the full-width at half maximum (FWHM) of the most intense peak, θ is the Bragg's angle and λ is the wavelength of X-ray.

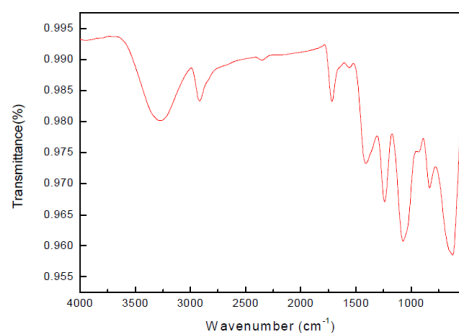


Figure 3 (a). IR Spectra of PVA-barium ferrite nanocomposites

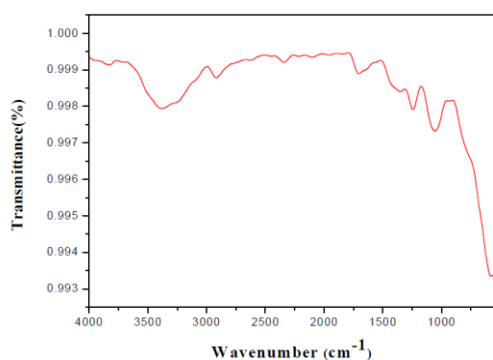


Figure 3(b). IR Spectra of PVA-nickel ferrite nanocomposites

3.5 Effect of Contact Time

The effect of contact time on the removal efficiency of copper, cadmium and lead ions using synthesized PVA- barium and PVA -nickel ferrite nanocomposites were studied at the interval of 30 min, at room temperature for 150 min is shown in the figure 5(a) & 5(b). It is observed from the result, that the removal of metal ions increases with increase in contact time and attained equilibrium, after which further increase in time did not bring about any further improvement for the removal of metal ions, but resulted in desorption of metal ions from the adsorbent surface.

PVA- barium ferrite nanocomposites shows maximum removal of 97.56%, 98.35%, 99.0% for Pb^{2+} , Cd^{2+} , Cu^{2+} respectively in 60min.

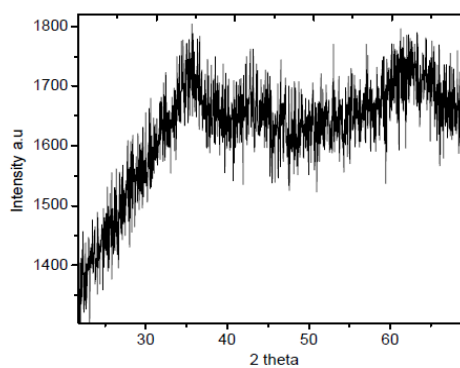


Figure 4 (a). XRD analysis of PVA-barium ferrite nanocomposites

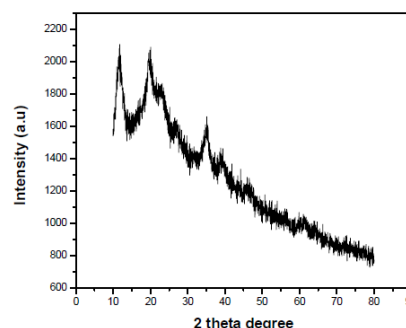


Figure 4 (b). XRD analysis of PVA-nickel ferrite nanocomposites

Whereas PVA- nickel ferrite nanocomposites shows maximum removal of 98.05% , 92.0% , 99.3 % for Pb^{2+} , Cd^{2+} , Cu^{2+} respectively in 90 min. The results shows that the different metal ions attained equilibrium at different times and the higher removal efficiency is for the removal of Pb^{2+} , and lower removal efficiency is for the removal of Cd^{2+} .

3.6 Effect of Adsorbent Dosage

The availability and accessibility of adsorption site is controlled by adsorbent dosage. Adsorbent dosage was varied from 0.05 to 0.20 g, under the specific condition (contact time of 150 min, 120 rpm shaking speed and room temperature and pH of 6) using the adsorbent PVA-barium ferrite and PVA-nickel ferrite nanocomposites. It is noticed from the figure 6(a) & 6(b) that the increase in adsorbent dosage.

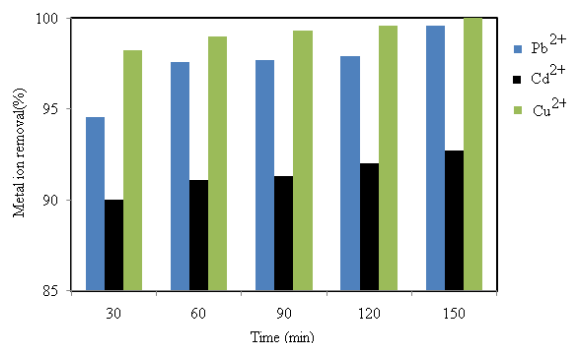


Figure 5(a). Effect of contact time on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; Agitation speed:120rpm;dsorbent dose: 0.1 g; pH:6. Adsorbent: PVA- barium ferrite nano composites

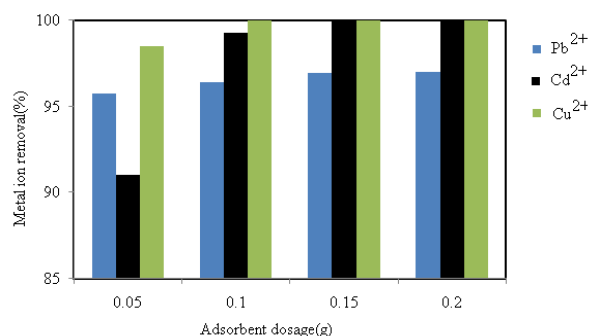


Figure 6(a). Effect of adsorbent dosage on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; Agitation speed:120 rpm; contact time: 150min; pH:6. Adsorbent: PVA-barium ferrite nanocomposites

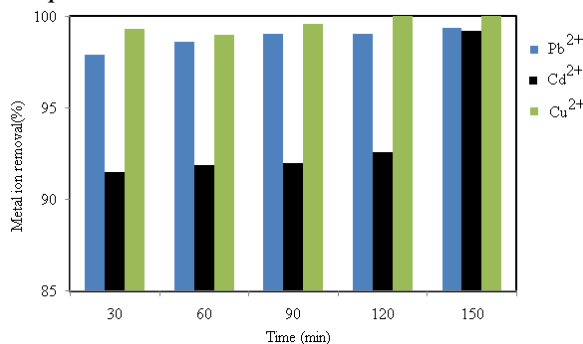


Figure 5 (b). Effect of contact time on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; Agitation speed:120rpm;dsorbent dose: 0.1 g; pH:6. Adsorbent: PVA-nickel ferrite nano composites

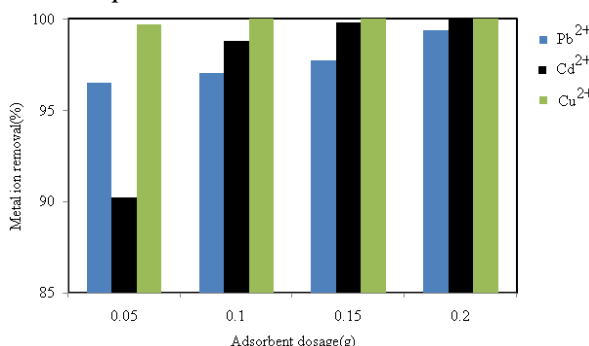


Figure 6(b). Effect of adsorbent dosage on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; Agitation speed:120rpm;contact time:150min; pH:6. Adsorbent: PVA-nickel ferrite nano composites

Also increases the removal efficiency of metal ions and maximum removal efficiency was attained at a particular adsorbent dosage, after which further increase in adsorbent dosage, brought no increase in adsorption, which was as a result of overlapping of adsorption sites due to overcrowding of adsorbent particles. PVA- barium ferrite nanocomposites shows maximum removal of 96.43%, 99.3%, 100% for Pb²⁺, Cd²⁺, Cu²⁺ respectively which was observed for 0.1 g of adsorbent dosage, where as PVA-Nickel ferrite nanocomposites shows maximum removal of 97.03%, 98.8%, 100% for Pb²⁺, Cd²⁺, Cu²⁺ respectively for 0.1 g of adsorbent dosage.

3.7 Effect of pH

The effect of pH was studied from a range of 2 to 8 under the precise conditions (at optimum contact time 150 min, 120 rpm shaking speed, with 0.1g of the adsorbent used and at room temperature) is shown in the figure7(a)& 7(b). It is observed that with increase in the pH from 2 to 8 of the simulated industrial waste water, the removal efficiencies of Pb²⁺, Cd²⁺ and Cu²⁺ increased up to pH of 8 and maximum removal efficiency was obtained at pH 6 for both PVA-barium and PVA-nickel ferrite nanocomposites. Above pH 4, there was no change in removal efficiency of Copper and the removal efficiency of cadmium was gradually decreased. The maximum removal

efficiency of Pb^{2+} was obtained at pH 6 and above pH 4, there was no change in removal efficiency for PVA -barium ferrite nanocomposites. But, slight decrease in removal efficiency was observed for PVA -nickel ferrite nanocomposites. Barium ferrite nanoparticles PVA composite shows maximum removal efficiency of 96.28% for Pb^{2+} ions at pH 6, 92.5% for Cd^{2+} ions at pH 6, 99.1% for Cu^{2+} ions at pH 6 whereas nickel ferrite nanoparticles PVA composite shows maximum removal efficiency of 97.0% for Pb^{2+} ions at pH 6, 92.5 % for Cd^{2+} ions at pH 4, 99.6 % for Cu^{2+} ions at pH 4, for 0.1 g of adsorbent dosage. The effect of pH shows that PVA nanocomposites working well over the wide range of pH.

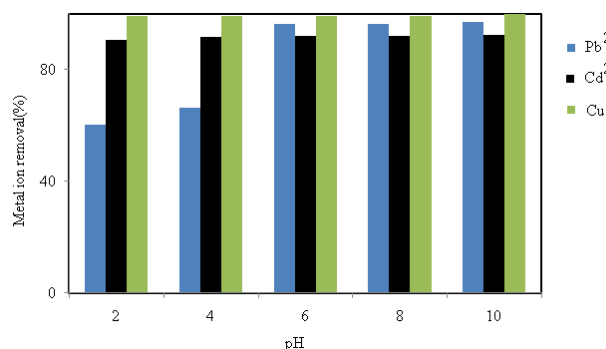


Figure 7(a) Effect of pH on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; Agitation speed:120 rpm; Adsorbent dose: 0.1 g; Contact time:150 min. Adsorbent: PVA-barium ferrite nanocomposites.

4. ADSORPTION ISOTHERM

The method of an adsorption system was optimized to remove the heavy metals with PVA -barium and PVA- nickel ferrite nanocomposites the most appropriate, correlations from the equilibrium data for each system. Two isotherm models that have been considered in the present study are Freundlich, Langmuir models. The applicability of the isotherm equations is evaluated by comparing the correlation coefficient R^2 .

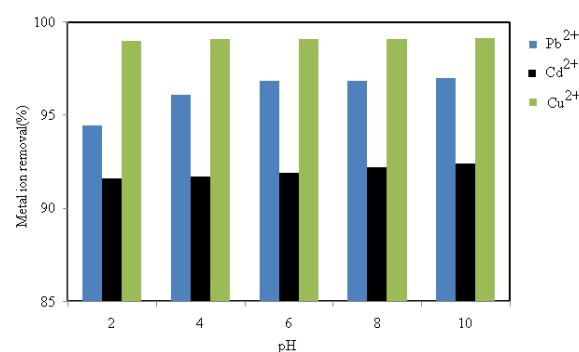


Figure 7(b). Effect of pH on adsorption of Lead, Cadmium, Copper. Temperature: 30°C; agitation speed:120rpm; Adsorbent dose: 0.1 g; Contact time :150min; Adsorbent: PVA-nickel ferrite nanocomposites

4.1 Freundlich Model

Freundlich isotherm is based on the multilayer adsorption with heterogeneous surface energies. The Freundlich adsorption isotherm model is widely used to explain the adsorption of heavy metals on a wide variety of adsorbent. It is an empirical equation that can be used for non-ideal sorption that involves heterogeneous sorption. The empirical model was shown to be consistent with an exponential distribution of active centers, characteristic of heterogeneous surface. The amount of solute adsorbed, Q_e is related to the equilibrium concentration of solute in solution, C_e as following [27],

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (5)$$

This expression can be linearized to give the following equation:

$$\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad (6)$$

Where, K_F is a constant for the system, related to the quantity of metal ion adsorbed onto adsorbent at an equilibrium concentration [or adsorption capacity, $mg\ g^{-1}$]. The values are plotted between $\log Q_e$ vs $\log C_e$. The values of K_F and $1/n$ are determined from the intercept and slope of the linear equation. Experimental data obtained were fitted into Freundlich adsorption isotherm is shown in the Table1. It is observed from the Table, the slope $1/n$, ranging between 0 and 1, is a measure of adsorption intensity or surface

heterogeneity [becoming more heterogeneous as its value gets closer to zero]. A value for $1/n$ below one indicates a normal Freundlich isotherm while $1/n$ above one is an indicative of cooperative adsorption.

4.2 Langmuir Model

Langmuir isotherm model mainly based on the assumption that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface. The Langmuir adsorption isotherm has been greatly used to many ground water effluent treatment processes and it has also been used to explain the adsorption of heavy metals by various adsorbents. Langmuir theory tells that adsorption takes place at specific homogeneous sites within the adsorbent. It is then assumed that once a metal ion molecule occupies a site after that no adsorption takes place adsorbent sites and adsorbed layer was unimolecular. The theory can be represented by the following linear form[28]

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (7)$$

The Langmuir isotherm can fit the experimental data better due to the relatively high ambient temperature that allowed only monolayer adsorption to occur. The van der Waals force that forms multilayer adsorption was overcome by the adsorbate due to the high ambient temperature. With relatively high room temperature, where the adsorption process occurs, the chemisorption was more dominant as compared to the physisorption. The relatively high room temperature cause the chemical bond to occur between the metal ions. Furthermore desorption will also occur between adsorbate and activated carbon at high temperature which physically bonded by the van der Waals force. Adsorbate which are physically adsorbed onto PVA- BFN composite and PVA- NFN composite receive sufficient energy from such high temperature to overcome the van der

Waals force. The graphs (C_e/q_e) vs. (C_e) were plotted for heavy metal Pb(II), Cd(II) Cu(II) in order to determine the Langmuir constant as shown in the Table 1.it was found that the Langmuir adsorption isotherm fitted the experimental data well. The adsorption capacity of adsorbent is compared with literatures presented in the Table 2 [29-34], which has considerable adsorption capacity for the present synthesized nanocomposites material.

5. CONCLUSION

The synthesized PVA-ferrite nanocomposites were used for the removal of heavy metals from simulated industrial wastewater. The experimental operating parameters such as adsorbent dosage, pH and contact time on adsorption has been optimized for maximum adsorption of metal ions. The removal efficiency and adsorption capacity of synthesized PVA-nano ferrite nanocomposites in removing copper, cadmium and lead were compared. PVA-barium and PVA-nickel ferrite nanocomposites an adsorbents, both shows higher removal efficiency for Cu^{2+} with 100% and 99.05% respectively. A PVA-barium ferrite nanocomposite shows lower removal efficiency for Cd^{2+} with 91.2 %; a PVA-nickel ferrite nanocomposite shows lower removal efficiency for Pb^{2+} with 83.47%. Adsorption Isotherm of Freundlich and Langmuir model parameters were determined and reported for the composite. The synthesized nanocomposites have greater potential for adsorption of heavy metal ions present in simulated industrial wastewater. These nanoparticles with polymeric composite can be effectively used as adsorbents in the commercial scale to achieve the desired goal of clean environment.

Table 1. Adsorption isotherm of Freundlich and Langmuir constants

Metal ions	PVA- Barium Ferrite Nanoparticle					
	Freundlich isotherm			Langmuir isotherm		
	1/n	K _F (mg g ⁻¹)	R ²	b	Q _m (mg g ⁻¹)	R ²
Pb ²⁺	0.4424	2.2603	0.9620	2.4808	3.9635	0.9689
Cd ²⁺	0.4131	1.3002	0.9953	1.5541	2.5050	0.9965
Cu ²⁺	0.5166	1.9357	0.9810	0.60397	4.0551	0.9945
PVA-Nickel Ferrite Nanoparticle						
Pb ²⁺	0.1636	6.1125	0.997	0.4128	4.66200	0.9784
Cd ²⁺	0.4119	2.4274	0.9970	1.0851	1.0691	0.9668
Cu ²⁺	0.7732	2.2685	0.9934	0.6085	4.1385	0.9633

Table 2 Adsorption capacities of Pb(II) ions with different types of adsorbents

Adsorbent used	Adsorption capacity (mg/g)	Ref
Ti(IV) iodovanadate cation exchanger	18.8	[29]
Rosa Canina-L leaves ash	25	[30]
Iron nano particle loaded ash	30	[30]
SDS-AZS	21.01	[31]
Mesoporous adsorbent	200.80	[32]
AC-R	5.35	[33]
Anatase nano adsorbent	31.25	[34]
PVA- Barium Ferrite Nanoparticle	2.26	Present study
PVA-Nickel Ferrite Nanaoparticle	6.11	Present study

REFERENCES

1. Nagajyoti, P. C., Lee, K. D., Sreekanth T. V. M., (2010). "Heavy metals, occurrence and toxicity for plants: A review", *Environ. Chem. Lett.*, 8: 199–216.
2. Jan, A. T., Murtaza, I., Ali, A., Haq, Q. M. R., (2009). "Mercury pollution: An emerging problem and potential bacterial remediation strategies", *World J. Microbiol. Biotechnol.*, 25: 1529–1537.
3. Clarkson, T. W. (1993). "Mercury:Major issues in environmental health", *Environ. Health Perspect.*, 100: 31–38.
4. Jalali, M., Khanlari, Z. V., (2008). "Environmental contamination of Zn, Cd, Ni, Cu and Pb from industrial areas in Hamadan Province, western Iran", *Environ. Geol.*, 55: 1537–1543 .

5. Peng, C., Liu, Y., Bi, J., Xu, H., Ahmed, A-S., (2011). "Recovery of copper and water from copper-electroplating wastewater by the combination process of electrolysis and electrodialysis", *Journal of Hazardous materials*, 189: 814-820.
6. Morrow, H., (2001). "Environmental and human health impact assessments of battery systems", *Industrial Chemistry Library*, 10: 1-34.
7. Aoun, M., Samrani, A. G., El Lartiges, B. S., Kazpard, V., Saad, Z., (2010). "Releases of phosphate fertilizer industry in the surrounding environment: Investigation on heavy metals and polonium-210 in soil", *Journal of Environmental Sciences*, 22: 1387-1397.
8. Malekirad, A. A., Oryan, S., Fani, A., Babapor, V., Hashemi, M., Baeeri, M., Bayrami Z., Abdollahi, M., (2010). "Study on clinical and biochemical toxicity biomarkers in a zinc-lead mine workers", *Toxicol. Ind. Health*, 26: 331-337.
9. Ji, W., Yang, T., Ma, S., Ni, W., (2012). "Heavy Metal Pollution of Soils in the Site of a Retired Paint and Ink Factory", *Energy Procedia*, 16: 21-26.
10. Huang, Y., Zeng, X., Guo, L., Lan, J., Zhang, L., Cao, D., (2018). "Heavy metal ion removal of wastewater by zeolite-imidazolate frame works", *Separation and Purification Technology*, 194:462-469.
11. Erwin, B., Montgomery, J., (1995) "Heavy metals and the etiology of Parkinson's disease and other movement disorders", *Toxicology*, 97: 3-9.
12. Michael Caudle, W., Guillot, T. S., Lazo, C. R., Miller, G. W., (2012). "Industrial toxicants and Parkinson's disease", *Neuro Toxicology*, 33: 178-188.
13. Tran, T-K., Chiu, K-F., Lin, C-Y., Leu, H-J., (2017). "Electrochemical treatment of wastewater: Selectivity of the heavy metals removal process", *International Journal of Hydrogen Energy*, 42: 27741-27748.
14. Taseidifar, M., Makavipour, F, Pashley, R. M., Mokhlesur Rahman, A. F. M., (2017). "Removal of heavy metal ions from water using ion flotation", *Environmental Technology & Innovation*, 8: 182-190.
15. Othman, Z. A. A., Alam, M. M., Naushad, M., (2013). "Heavy toxic metal ion exchange kinetics: Validation of ion exchange process on composite cation exchanger nylon 6,6 Zr(IV) phosphate", *Journal of Industrial and Engineering Chemistry*, 19: 956-960.
16. Vázquez, G., Calvo, M., Sonia Freire, M., González-Alvarez, J., Antorrena, G., (2009). "Chestnutshell as heavy metal adsorbent: optimization study of lead, copper and zinc cations removal", *J. Hazard. Mater.*, 172: 1402-1414.
17. Homaga, P. L., Inoue, K., (2010). "Adsorption behavior of heavy metals onto chemically modified sugarcane bagasse", *Bioresource Technology*, 101: 2067-2069.
18. Shukla, S. R., Pai, R. S., Shendarkar A. D. (2006) "Adsorption of Ni (II), Zn (II) and Fe (II) on modified coir fibre", *Sep. Purif. Technol.*, 47: 141-147.
19. Periasamy, K, Namasivayam, C., (1995). "Removal of nickel (II) from aqueous solution wastewater using an agricultural waste: peanut hulls", *Waste Manage.*, 15: 63-68.
20. Singh, R. S., Singh V. K., Tiwari, P. N., Singh U. N., Sharma, Y. C., (2009). "An economic removal of Ni (II) from aqueous solutions using an indigenous adsorbent", *Open Environ. Eng. J.*, 2: 30-36.
21. Kadirvelu, K., Thamaraiselvi, K., Namasivayam, C., (2001). "Removal of heavy metal from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste", *Bioresour. Technol.*, 76: 63-65.
22. Alqadami, A. A., Naushad, M., Abdalla, M. A., Ahamad, T., AlOthman, Z.A., Alshehri, S. M. Ghfar A. A., (2017). "Efficient removal of toxic metal ions from wastewater using a recyclable nanocomposite: A study of adsorption parameters and interaction mechanism", *Journal of Cleaner Production*, 156: 426-436.
23. Alqadami, A. A., Naushad, M., AlOthman, Z. A., Ghfar, A. A., (2017). "Novel Metal-Organic Framework (MOF) Based Composite Material for the Sequestration of U(VI) and Th(IV) Metal Ions from Aqueous Environment", *ACS Appl. Mater. Interfaces*, 9: 36026-36037.
24. Shahat, A., Awual, M. R., Khaleque, M. A., Alam, M. Z., Naushad, M., Sarwaruddin Chowdhury, A.M., (2015). "Large-pore diameter nano-adsorbent and its application for rapid lead(II) detection and removal from aqueous media", *Chemical Engineering Journal*, 273: 286-295.
25. Mironyuk, I., Tatarchuk, T., Naushad, M., Vasylyeva, H., Mykytyn, I., (2019). "Highly efficient adsorption of strontium ions by carbonated, mesoporous TiO₂", *Journal of Molecular Liquids*, 285: 742-753.
26. Kefeni, K. K., Msagati, T. A. M., Mamba, B.B., (2017). "Ferrite nanoparticles: Synthesis, characterisation and applications in electronic device", *Materials Science and Engineering: B*, 215: 37-55.
27. Murugesan, A., Ravikumar, L., SathyaSelvaBala, V., SenthilKumar, P., Vidhyadevi, T., Dinesh Kirupha, S., Kalaivani, S., Krithiga, S., Sivanesan, S., (2011). "Removal of Pb(II), Cu(II) and Cd(II) ions from aqueous solution using polyazomethineamides: Equilibrium and kinetic approach", *Desalination*, 271: 199-208.
28. Gunasundari, E., Senthil Kumar, P., (2017). "Adsorption isotherm, kinetics and thermodynamic analysis of Cu (II) ions onto the dried algal biomass (*Spirulina platensis*)", *Journal of Industrial and Engineering Chemistry*, 56: 129-144.

29. Naushad, M., ALOthman, Z. A. Awual, M. R. Alam, M. M., Eldesoky, G. E., (2015). "Adsorption kinetics, isotherms, and thermodynamic studies for the adsorption of Pb^{2+} and Hg^{2+} metal ions from aqueous medium using Ti(IV) iodovanadate cation exchanger", *Ionics*, 21:2237–2245.
30. Ghasemi, M., Naushad, M., Ghasemi, N., Khosravi-fard, Y., (2014). "Adsorption of Pb(II) from aqueous solution using new adsorbents prepared from agricultural waste: Adsorption isotherm and kinetic studies", *Journal of Industrial and Engineering Chemistry*, 20: 2193–2199.
31. Naushad, M., (2014). "Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium", *Chem. Eng. J.*, 235: 100–108.
32. Awual, M. R., Hasan, M. M., Shahat, A., (2014). "Functionalized novel mesoporous adsorbent for selective lead(II) ions monitoring and removal from wastewater", *Sens. Actuators B: Chem.*, 203: 854–863.
33. Lalmunsiana, Lee, S. M., Tiwari, D., (2013). "Manganese oxide immobilized activated carbons in the remediation of aqueous wastes contaminated with copper(II) and lead(II)", *Chem. Eng. J.*, 225: 128–137.
34. Atakli, Z. O. K. Yurum, Y., (2013). "Synthesis and characterization of anatase nanoadsorbent and application in removal of lead, copper and arsenic from water", *Chem. Eng. J.*, 225: 625–635