

Enhanced removal of Ni(II) from electroplating effluents using herbal biomass as alum substituents

Rakhee Bhagavath^a, Supriya Subrahmanian^{a,*}, Narendrakumar G.^b

^aDepartment of Chemistry, Sathyabama Institute of Science and Technology, Jeppiaar Nagar, Chennai – 600119, Tamil Nadu, India, emails: rakheebhagavath@gmail.com (R. Bhagavath), supriyasubrahmani@gmail.com (S. Subrahmanian)

^bDepartment of Biotechnology, Sathyabama Institute of Science and Technology, Jeppiaar Nagar, Chennai – 600119, Tamil Nadu, India, email: gnaren22@gmail.com

Received 17 May 2021; Accepted 22 October 2021

ABSTRACT

The study focuses on the coagulation/flocculation (C/F) property of the biomass extracts from *Ficus religiosa*, *Annona squamosa*, *Murraya koenigii* and *Opuntia ficus-indica*. The biomass was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy with energy dispersive X-ray spectrophotometer (SEM-EDAX) and zeta potential values. The performance of the four biomass materials in the removal of Ni(II) ions from the electroplating effluents have been investigated. Based on their response with synthetic wastewater, the treatment process was successfully applied for the treatment of the electroplating effluents. Results obtained showed the maximum Ni(II) removal efficiency of the biomass extracts as 45% under acidic pH, 63% under neutral pH, and 81% under alkaline pH conditions. The optimized condition required for achieving 90% removal of the nickel ions from the electroplating effluents was obtained from Box–Behnken–Design (BBD), using pH, dosage of flocculants, and concentration of nickel as independent variables whereas turbidity, sedimentation, and Ni(II) removal (%) as response variables. Desirable results were obtained at pH value of 8.5 and 1.5 g/L of biomass dosage of *A. squamosa*. The treated effluent has to subsequently undergo biological treatment in order to meet the discharge standards. In the primary wastewater treatment with biomass extracts, Ni(II) removal efficiency was comparable to that of the alum usage and is attained by the use of non-toxic biodegradable coagulants.

Keywords: Biomass extract; Electroplating effluent; Nickel; *Ficus religiosa*; *Annona squamosa*; *Murraya koenigii* and *Opuntia ficus-indica*; Box–Behnken–design

1. Introduction

Effluents from electroplating industries have high concentrations of heavy metals which are hazardous in nature. Due to their high level of toxicity, treatment of these effluents has become mandatory before their discharge into the environment. Cutting edge innovative technologies are being adopted in electroplating industries, leading to salt recovery with zero discharge. But in developing countries, most of the small scale plating industries still follow the conventional method of production, where there is

continuous discharge of the effluents containing high concentrations of metals. Many treatment methods like chemical precipitation, coagulation/flocculation (C/F), membrane filtration, ion-exchange, adsorption etc., have been extensively used as promising methods by these industries over the years [1]. Currently, advanced treatment methods such as membrane technology, nano-filtration, electrocoagulation, photo-catalysis, and ozonation methods are also additionally being employed in industries. Among the conventional methods, precipitation is the most basic and economical method of treatment. It is being done by the addition of alkali and alum which are capable of removing

* Corresponding author.

colloidal matters by the process of coagulation in the form of gelatinous hydroxides [2]. Lime/Ca(OH)₂ is the primary substance used in most of the treatment plants for the precipitation of high concentrations of suspended solids. Nearly, 50 kg of lime is required for the treatment of every 1,000 KL of the effluent. Usage of lime has resulted in heavy sludge formation [3] and has also caused disposal problems. Hence a preferred alternative treatment method is the C/F process for the effluents containing high metal ion concentrations. Conventional chemicals used for this method are lime Ca(OH)₂, alum (AlSO₄), and polyelectrolytes (cationic or anionic). The effectiveness of these chemicals have been well-established by various studies. In spite of specific detriments like high procurement cost and high volume of hazardous sludge formation due to the presence of aluminium, C/F still remains as the most desirable treatment method. However, aluminium based coagulants have been linked to the raise in Alzheimer's disease in humans as per reports [4]. Due to the hazardous nature of these chemicals and their tendency to pollute the environment, their replacement has now become inevitable and must be given the utmost importance.

Recently, extensive research has been carried out on plant based coagulants. The past decade has seen the utilization of many natural coagulants such as Nirmali seeds (*Strychnos potatorum*), *Moringa oleifera*, coconut, tannin etc., for water treatments and removal of turbidity [5]. These substances have been largely used by rural communities for the treatment of water for many centuries. This concept has now been extended to the treatment of industrial effluents. Many such studies have been conducted for the removal of heavy metals from industrial effluents using naturally occurring materials, such as olive stone [6], *Tectona grandis* (teak) [7], sorghum bicolor [8], coconut coprameal [9], and cassava peel [10]. In this study, we have taken the biomass (leaves) of *Ficus religiosa* (pipal), *Annona squamosa* (sugar apple/ S. Apple), *Murraya koenigii* (curry), and *Opuntia ficus-indica* (cactus) for the removal of Ni(II) ions from the electroplating effluents. For the removal of metals from the electroplating effluent using natural materials, the common method adopted was the principle of adsorption [11]. Similarly, removal of Ni(II) ions through adsorption on biomass have also been extensively studied and are reported [12,13]. Here, we have explored the C/F properties of four biomass materials and their efficacy in replacing alum. Among the four biomass materials selected, *O. ficus-indica* is a well-established natural coagulant [14] and has also been used for the treatment of paint effluents [15]. *A. squamosa* [16,17] and *F. religiosa* [18] have been broadly used as adsorbents. *M. koenigii* [19] find wide applications in the research field for its medicinal properties. Studies on the utilization of biomass material for the treatment of effluents and as alum substituents, which are worthy of exploration, are inadequate. The C/F processes using chemicals have always been a preferred primary treatment method for inorganic effluents and have played a key role in the removal of heavy metals [20], where they are generally precipitated as their hydroxides [21]. In this study, plant leaves, which are biodegradable and cost-effective due to their regional availability, are used as alum substituents in order to enhance the percentage of metal removal. The objective of this study is to

analyze the role of biomass materials as alum substituents in the treatment of electroplating effluents and to optimize the condition in terms of pH, dosage, and metal ion concentration for the maximum removal of Ni(II) ions using Box–Behnken–design (BBD).

2. Materials and methods

2.1. Biomass preparation

The leaves of *F. religiosa*, *A. squamosa*, *M. koenigii*, and *O. ficus-indica* were collected from the residential area of New Perungalathur located in Chennai. They were washed separately under running tap water and rinsed well with distilled water. This biomass was dried under the sun for nearly 48 h and was placed in a hot air oven at 105°C for 2 h. The biomass was then finely ground with the help of a blender. The powdered particles were sieved through a 80–100 mesh. These powdered leaf materials were stored in an airtight container for future use. For the preparation of the biomass extract, 50 g of the powdered leaf was weighed and taken in a 1 L standard flask. To this 1,000 mL of distilled water was added. The leaf was soaked in distilled water for 48 h and then filtered. The 5% solution of the biomass extract thus prepared was stored at 4°C for further study.

2.2. Biomass characterization

2.2.1. Scanning electron microscopy

The surface morphology of the prepared biomass powder was studied using a scanning electron microscopy (SEM) attached with an energy dispersive X-ray spectrophotometer (Carl Zeiss NTS GMBH, Germany SUPRA 55).

2.2.2. Fourier transform infrared spectroscopy

The infrared spectra of the biomass was obtained using an ALPHA spectrophotometer Bruker OPUS model instrument.

2.2.3. Inductively coupled plasma – optical emission spectrometry

Metal ion concentrations of the untreated and treated effluents were determined using inductively coupled plasma – optical emission spectrometry (ICP-OES) instrument of model Perkin Elmer Optima 5300 DV.

2.2.4. Zeta potential

Zeta potential of the 5% solution of the biomass extracts was determined and the data was obtained using a dynamic light scattering – particle size and zeta potential analyzer of model: Nanotracs Wave II, Microtrac, Inc., USA.

2.3. Untreated effluent

2.3.1. Preparation of synthetic effluent

Weighed exactly the mole ratios of the analar grade nickel nitrate (Ni(NO₃)₂·6H₂O) salt and dissolved them completely in distilled water in a 1 L volumetric flask.

2.3.2. Electroplating effluent

An electroplating industry located in Ambattur Industrial Area of Chennai was selected for the collection of the untreated effluent. In this factory, zinc and nickel electroplating processes are carried out on a regular basis. For the purpose of our study, nickel effluent samples were collected from the rinsing tanks, where the plated objects are being rinsed after completion of the electroplating process. The study was performed using 10 L volume of the effluent named as acid nickel.

The general treatment procedure adopted for the removal of heavy metals present in the industrial effluents involves the application of chemical treatment. Here, heavy metals are typically removed by precipitation in the form of their hydroxides by neutralization of the effluents with NaOH in accordance with the following equation:



2.4. Characterization of the electrochemical effluents

Physicochemical characterization of the effluent was carried out in an NABL accredited laboratory as per the analytical methods listed in IS 3025. Estimation of metals in the test solution was done by ICP-OES instrument. Treatment of the effluent by C/F process was carried out in a Jar test apparatus as per the ASTM standard: D 2035-08. Magnetic stirrers were used to bring about efficient adsorption and the results are given in Table 1.

2.5. Chemicals

Analar grade chemicals were used for the study. NaOH and HCl were used for maintaining the pH of the synthetic effluents. Sodium hydroxide, calcium hydroxide, alum, or aluminum sulfate were used for precipitation and for the C/F processes.

2.6. Jar test method

Treatment of each sample was performed by Jar test method as per IS 3025 part 50. For every trial, 500 mL of the

sample was taken in a 1 L beaker into which the required quantity of the biomass extract was added. The beaker was then placed in a jar test apparatus and mixed rapidly for 2 min at 100 rpm, followed by slow mixing for 15 min at 40 rpm. This solution was then allowed to settle for 30 min after which the supernatant liquid was analyzed for its composition. All the treatment steps were carried out in triplicates to minimize the error and the mean value of the results obtained were recorded.

2.7. Response surface methodology

Based on the preceding analysis, it was found that the pH, concentration of nickel, and dosage of flocculants are the major variables in sedimentation, Ni(II) removal percentage and turbidity, keeping all other parameters as constants. The statistical experimental design using Design expert version 7.0, Stat-Ease, Minneapolis was used for optimization. This method involves a number of empirical techniques to evaluate the correlation of experimental factors and predict the critical concentration of dependent and independent variables. A BBD was employed to obtain the experimental data that fits in full quadratic polynomial design, signifying the response surface over a comparatively broad range of parameters. The range and the levels of experimental variables examined are shown in Table 2.

The quadratic equation is:

$$\pi = \pi_0 + \pi_1 A + \pi_2 B + \pi_3 C + \pi_4 A^2 + \pi_5 B^2 + \pi_6 C^2 + \pi_7 AB + \pi_8 BC + \pi_9 AC \quad (2)$$

where Y is the measured response, A , B , and C are the coded independent input variables, π_0 is the intercept term, π_1 , π_2 , and π_3 are the coefficients showing the linear effects, π_4 , π_5 , and π_6 are the quadratic coefficients showing the squared effects and π_7 , π_8 , and π_9 are the cross product coefficients showing the interaction effects.

3. Results and discussion

3.1. Effect of pH

pH plays an important role in the removal of metal ions, as it influences the chemistry of metal ion binding with the

Table 1
Chemical analysis result of the untreated effluent

S. no	Parameters	Nickel (acid effluent)	Synthetic effluent	Measurement uncertainty (\pm) at value
(1)	pH	4.36	4.28	8.244 ± 0.101
(2)	Electrical conductivity, $\mu\text{S}/\text{cm}$	5,40	860	$0.002 \pm 102.3 \mu\text{S}/\text{cm}$
(3)	Turbidity, NTU	2,475	52	$0.5 \pm 1.80 \text{ NTU}$
(4)	Total dissolved solids, mg/L	3,256	586	$1,521 \pm 6$
(5)	Chemical oxygen demand, mg/L	1,262	ND	$198,400 \pm 3,201$
(6)	Biological oxygen demand, mg/L	380	ND	768 ± 16.01
(7)	Total chromium, mg/L	2.94	ND	$0.18 \pm 0.005 \text{ ppm}$
(8)	Iron, mg/L	2.4	ND	$0.0299 \pm 0.21 \text{ mg/L}$
(9)	Nickel, mg/L	1,697	204	$0.09 \pm 0.0061 \text{ ppm}$
(10)	Zinc, mg/L	18.96	ND	$0.184 \pm 0.005 \text{ ppm}$
(11)	Manganese, mg/L	0.232	ND	$0.014 \pm 0.20 \text{ mg/L}$
(12)	Copper, mg/L	0.85	ND	$0.074 \pm 0.0012 \text{ ppm}$

ND – not detected.

Table 2
Observed and predicted values for sedimentation, Ni(II) removal percentage and turbidity

Std	A: pH	B: Dosage of flocculants	C: Concentration of nickel	Sedimentation		Ni(II) removal percentage		Turbidity	
				Actual	Predicted	Actual	Predicted	Actual	Predicted
12	8	3	1700	0.07	0.06	30.9	31.8	3,002	2,985
4	9	3	950	0.12	0.12	31.6	31.4	2,838	3,002
1	7	0	950	0.09	0.09	23.2	23.4	3,446	3,282
2	9	0	950	0.54	0.52	51.2	52.2	2,068	1,899
8	9	1.5	1700	0.17	0.19	52.6	51.9	2,608	2,461
16	8	1.5	950	0.94	0.92	90.2	90.2	60.7	63
11	8	0	1700	0.15	0.16	45.2	44.9	2,815	3,131
6	9	1.5	200	0.21	0.22	50.3	50.1	1,693	1,845
17	8	1.5	950	0.92	0.92	91.3	90.2	64.1	63
3	7	3	950	0.23	0.25	49.6	48.6	1,509	1,678
14	8	1.5	950	0.92	0.92	90.1	90.2	63.4	63
10	8	3	200	0.07	0.06	43.6	43.9	3,027	2,711
15	8	1.5	950	0.93	0.92	90.2	90.2	61.2	63
5	7	1.5	200	0.08	0.07	42.2	42.9	2,175	2,322
13	8	1.5	950	0.91	0.92	89.3	90.2	63.2	63
9	8	0	200	0.19	0.20	27.2	26.4	3,048	3,066
7	7	1.5	1700	0.06	0.05	47.3	47.5	2,195	2,043

substrate [8]. At lower pHs, there is more competition for the binding sites by both metal ions and protons, whereas at higher pH values, the negatively charged medium attracts more of the positively charged metal ions resulting in the removal of a higher percentage of metals [22]. pH optimization helps in the determination of the coagulant dosage requirements. For this study, synthetic effluent was used. The efficiency of all the four leaf extracts in the removal of Ni(II) metal ions from the effluent were determined. The results are given in Table 3.

3.1.1. Acidic medium

Nearly 10 g/L of the biomass was added to the synthetic effluent and the solution was stirred while being mounted on a Jar test apparatus. After the settling period, the supernatant solution was analyzed for the presence of nickel ions. It is found that the Ni(II) removal is in the range of 30%–45%. In this medium, the biomass of curry leaf is found to be more effective with 45% removal of Ni(II).

3.1.2. Neutral pH

After adjusting the pH of the synthetic effluent to 7 with 1 N NaOH, nearly 7.5 g/L of biomass was added to the solution and stirred. It is found that nearly 50% of Ni(II) removal is achieved for the synthetic effluent. In the neutral pH medium, biomass of Pipal leaf is found to be more effective compared to the other biomass materials.

3.1.3. Alkaline medium

Around 70%–80% of Ni(II) removal is achieved under alkaline pH condition for all the biomass materials. It is observed that the efficiency of Ni(II) removal for the test

sample is increasing with increasing pH for all the four biomass materials. The optimum pH for the removal of Ni(II) is found to be in the range of 8.0–8.5.

3.2. Characterization of the biomass material

3.2.1. Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) spectra of the four biomass materials *F. religiosa*, *A. squamosa*, *M. koenigii*, and *O. ficus-indica* are used for the study and the FTIR spectra of *A. squamosa* is provided in Fig. 1. The broad peaks observed between 3,342.74 and 3,428 cm^{-1} for all the leaves shows the presence of N–H groups. The sharp peaks observed from 2,921.97 to 2,923.84 cm^{-1} correspond to the C–H stretching frequency of the alkyl group. The small peaks observed in the range of 2,353.60 to 2,356.60 cm^{-1} , which is commonly observed for all the leaf extracts, correspond to C–H bending. The peaks between 1,614 to 1,634 cm^{-1} indicate the presence of C=O, whereas the peak at 1,623 cm^{-1} corresponds to N–H stretching and bending of the protein linkages [23]. The peaks between 1,063.39 and 1,067.23 cm^{-1} observed for the leaves indicate the presence of either C–O or S=O stretching vibrations. The peaks at 663 and 668 cm^{-1} correspond to the di-substituted C=C bending vibrations. The cluster of peaks present between 1,435 and 1,256 cm^{-1} represents C–O and O–H stretching vibrations. Hence, the peaks present in the FTIR spectrum confirms the presence of proteins and polysaccharides in the sample biomass.

3.2.2. Scanning electron microscopy

Fig. 2 represents the SEM image of *A. squamosa*. The asymmetric pores on the surface of the biomass material

Table 3
Removal of Ni ions at different pH values by biomass addition to synthetic effluent

S. no	Biomass addition	Medium of pH	pH	Nickel (mg/l)	Removal percentage
Reference	Synthetic effluent	Initial	4.28	204	–
(1)	Pipal	Acidic	4.5–5.5	132.14	35.22
		Neutral	6.5–7.5	86.02	57.83
		Alkaline	7.5–10	44.16	78.35
(2)	<i>Annona Squamosa</i>	Acidic	4.5–5.5	141.1	30.83
		Neutral	6.5–7.5	102.7	49.65
		Alkaline	7.5–10	57.12	72
(3)	Cactus	Acidic	4.5–5.5	136.5	33.08
		Neutral	6.5–7.5	92.24	54.78
		Alkaline	7.5–10	38.56	81.09
(4)	Curry	Acidic	4.5–5.5	111.21	45.48
		Neutral	6.5–7.5	94.11	53.86
		Alkaline	7.5–10	52.21	74.41

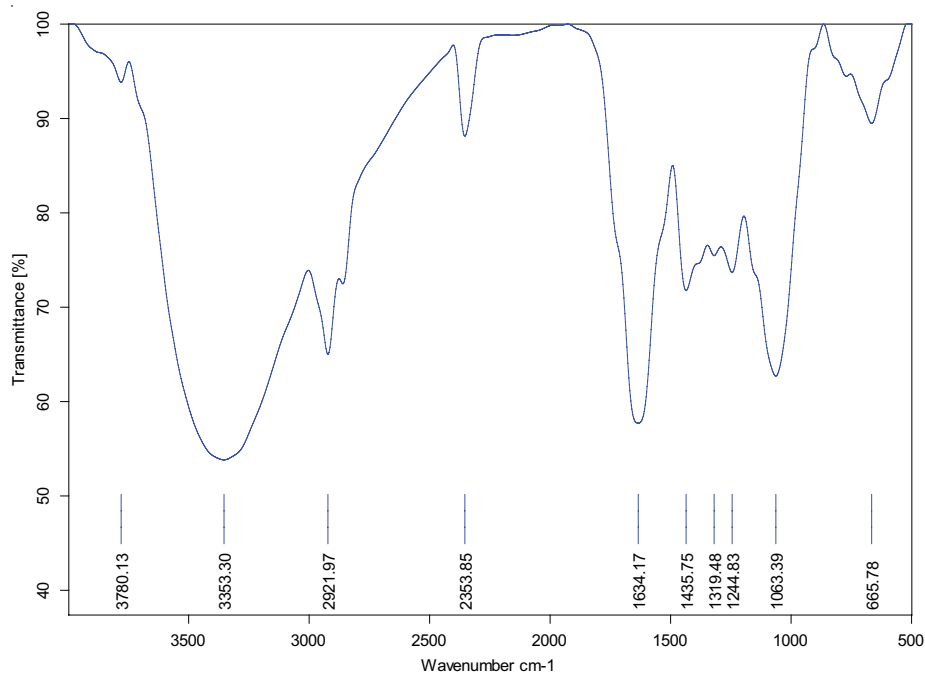


Fig. 1. FTIR spectrum of *Annona squamosa*.

act as binding sites for the Ni(II) metals ions. The surface morphology study by SEM shows a gelatinous and spherically layered continuous structure of the biomass materials. Both FTIR and SEM studies confirm the polymeric nature of the biomass materials.

3.2.3. Zeta potential

There is no coagulation – flocculation taking place during the treatment process when the biomass extract is added without the addition of lime to the electroplating wastewater. However, there is very good floc formation in the presence of lime. The ζ value of the untreated

nickel effluents is 38 mV. The ζ value of the different biomass extracts are as follows: pipal = 29.1 mV, curry leaf extract = 24.6 mV, sugar apple extract = 42.5 mV, and for cactus extract = 3.5 mV. Addition of these extracts to the electroplating wastewater, in the absence of lime, did not bring about any coagulation and the stability of the sample can be attributed to high ζ values. When the particles in the medium have ζ values greater than +30 mV or lower than –30 mV, the dispersion stability occurs due to their mutual repulsion [24]. But, when the biomass extract is added along with lime solution there is immediate onset of agglomeration of particles and hence there is very good C/F taking place in the pH range of 8–10. By the addition

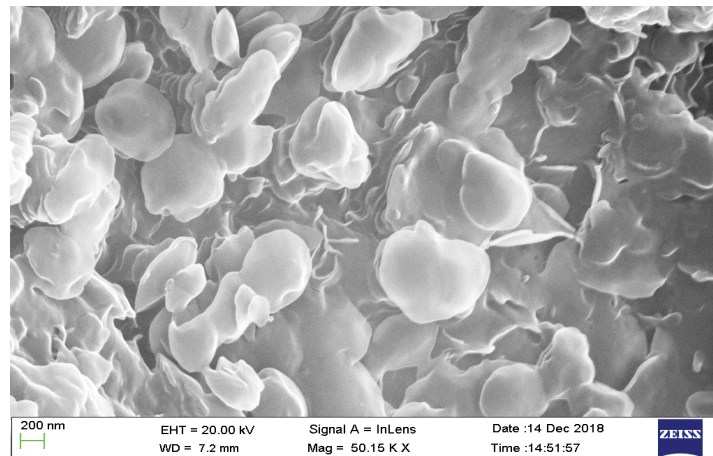


Fig. 2. SEM image of the *Ammonia squamosa*.

of $\text{Ca}(\text{OH})_2$, there is an increase in the negative charge as a result of high dissociation of H^+ ions from the functional groups of the biomass leading to flocculation.

3.3. Coagulation–Flocculation process

Coagulation process is generally defined as the removal of non-settleable solids by the addition of certain chemicals [25]. Temperature, pH, and contact time are the controlling factors for the coagulation process. Here acid nickel effluents from the electroplating industry and the synthetic effluent prepared in the laboratory were utilized for the study, which was conducted at a temperature of 30°C and with a contact time of 30 min. The coagulant dosages were varied for the optimization of the process. For all the dosages, a 5% solution of lime followed by 5% solution of alum were added to the sample and mixed rapidly for about 5 min at 100 rpm, followed by slow stirring for another 15 min. After a settling period of 30 min, the contents were taken for physicochemical analysis. This procedure was repeated with each of the biomass extract along with lime and without the use of alum in the C/F process. Thus the effectiveness of the four biomass extracts in the replacement of alum for the removal of Ni ions from the electroplating effluent was determined.

3.3.1. Dosage optimization

3.3.1.1. Synthetic effluent

Optimum dosage required for the removal of Ni(II) from the synthetic effluent using lime alum addition is 0.75 g/L

of lime and 0.15 g/L of alum. Replacement of alum with the biomass extract required 0.83 g/L of lime along with nearly the same amount of biomass, that is, 0.83 g/L. Here, 99% removal of Ni(II) from the effluent is observed as given in Table 4.

3.3.1.2. Acid nickel effluent

For the removal of nickel from the acid nickel effluent, 0.4 g/L of lime with 0.33 g/L of alum combination was required. In the presence of biomass extracts, the lime dosages required are as follows: 0.5 g/L of lime with 2.5 g/L of pipal extract, 0.5 g/L of lime with 1.5 g/L of S. Apple extract, 0.4 g/L of lime with 3.33 g/L of cactus and 0.4 g/L of lime with 1.16 g/L of the curry leaf extract. In all cases, nickel ion removal from the electroplating effluent is found to be 85% and above. The result of Ni(II) removal is given in Table 5.

3.3.2. Effect of lime addition on metal removal

An optimum dosage of 1 g/L of lime is found to be effective for the removal of 58% of Ni(II) from the acid nickel effluent. This is possible because of its good coagulation property. Addition of biomass extract along with lime shows enhanced metal removal. Good flocculation is also observed when the biomass extract is added along with lime. In the absence of lime, there is no C/F taking place and only adsorption is found to predominate. Adsorption is a surface phenomenon in which the metal ions are adsorbed on the biomass material. In the absence of lime addition,

Table 4
Synthetic effluent treatment

S. no	Parameters	U-SE	Addition of lime along with				
			Alum	Pipal	S. Apple	Cactus	Curry
(1)	pH	4.44	10.06	10.99	10.07	10.95	10.96
(2)	Nickel (mg/L)	204	0.19	0.22	0.13	0.16	0.36

U-SE = Untreated synthetic effluent

the metal removal efficiency of the biomass extract is poor and the color of the extract is retained in the supernatant liquid. Removal efficiency of the biomass in the absence of lime is presented in Table 3.

3.3.3. Effect of metal ion concentration

Ni(II) concentration in the untreated nickel effluent is 1,697 mg/L and the Ni(II) removal efficiency from the nickel effluent is around 88%–90%. The removal percentage of Ni(II) present in the primary treated effluent varies with the initial concentration of Ni(II) present in the untreated effluent. The optimum dosage of lime and biomass required for the removal of Ni(II) present in the untreated nickel effluents with different initial concentrations of Ni(II) are given in Table 6. From the results obtained, there is a clear indication that there is about 30% enhancement in the Ni(II) removal by the addition of biomass along with lime rather than that obtained with lime alone. Also, Ni(II) ion removal efficiency of the biomass extracts is found to increase with the decrease in the initial metal ion concentration of the untreated effluents. Even after the primary treatment process, the result obtained is not within the permissible discharge limit set by the statutory bodies, which again is a challenge and can be mitigated through dilution of the untreated nickel effluent.

3.3.4. Effect of biomass in C/F process

The characterization of the biomass materials with the help of FTIR and SEM EDAX establishes the presence of hydroxyl groups along the polysaccharide chain. Addition of high molecular weight compounds such as polymers

were found to be helpful in improving the efficiency of the coagulation process [26]. The biomass is generally made up of macromolecular structures with various functional groups attached to it. Thus, they either act as coagulants or as a coagulant aid. As coagulants, they attack and stabilize the charged particles by the process of adsorption and neutralization. When they function as a coagulant aid, they destabilize the particles with the help of their functional groups through inter particle bridging [26]. The coagulant properties of *Opuntia ficus indica* has been attributed to the presence of galacturonic acid [4]. Among the four selected biomass materials in this study, effective flocculation and formation of heavy flocs is observed with the addition of *F. religiosa* and *A. squamosa* extracts along with lime addition. This re-establishes the fact that natural organic compounds like biomass, possess the unique characteristics of producing dense flocs with much strength and good settling properties compared to inorganic materials [24]. Other indicators such as turbidity, sedimentation rate, and the settled sludge volume (SSV) of the treated effluent, for the following combinations with the coagulants, are discussed below:

- Only lime addition.
- Lime and alum addition.
- Lime with biomass of pipal extract.
- Lime with biomass of S. Apple extract.
- Lime with biomass of cactus extract.
- Lime with biomass of curry extract.

3.3.4.1. Sedimentation rate

Settling rate of the suspended solids after the treatment of acid nickel electroplating effluent with

Table 5
Nickel electroplating effluent treatment

S.No	Parameter	U-NE	Addition of lime along with					
			Lime	Alum	Pipal	T. Apple	Cactus	Curry
(1)	pH	4.36	8.02	8.09	8.41	8.35	8.37	8.09
(2)	Nickel (mg/L)	1,697	698	206	192	205	192	199

U-NE = Untreated Nickel electroplating effluent; BDL = Below detection level.

Table 6
Treatment of nickel effluent with *Ficus religiosa* and *Annona squamosa* extract

S. no	Initial Ni concentration (mg/L)	Final Ni concentration (mg/L)	Lime dosage (gm/L)	Biomass dosage (gm/L)	Removal of Ni (%)
(1)	1,983	530	1.25	1.5 (pipal)	73.2
(2)	1,983	644	1.25	1.6 (S. Apple)	67.5
(3)	1,697	698	1.5	–	58.8
(4)	1,697	192	0.5	2.5 (pipal)	88.6
(5)	1,697	205	0.5	1.66 (S. Apple)	87.9
(6)	1,487	654	1	–	56.0
(7)	1,487	162	1	2 (pipal)	89.7
(8)	991.5	87.6	0.5	1.25 (pipal)	91.2
(9)	991.5	98.6	0.5	1.6 (S. Apple)	90.0

various combinations of the coagulants are provided in Fig. 3. The average settling rate for the acid nickel effluent is around 0.83 m/min. The graph indicates that the sedimentation rate for the treatment involving lime along with the biomass extract is almost similar to that attained for the lime alum treatment.

3.3.4.2. Effect on turbidity

Turbidity is an important indicator of the effectiveness of the coagulation process, and also helps in identifying the optimum dosage requirements. Fig. 4 gives the turbidity of the acid nickel effluent with the addition of various dosages of the coagulants for the above listed combinations.

It is observed that the turbidity of the treated sample is drastically reduced and is found to be in the range of $<10 \pm 2$ NTU for all the treated samples. It is further observed that the turbidity of the sample is increasing upon addition of excess amount of lime or lime with alum as coagulants. But with the addition of biomass extracts with lime as the coagulant, the turbidity is found to remain constant even when more than the optimum dosage of the coagulant is added.

3.3.4.3. Settled sludge volume

The SSV is the space occupied by the sludge in one litre measuring cylinder, given as mL/L as shown in Fig. 5. SSV of the treated nickel effluent involving lime

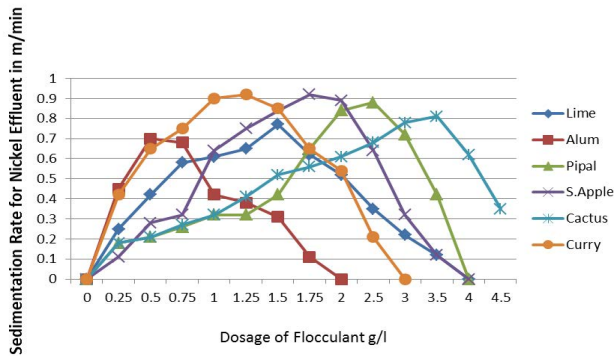


Fig. 3. Sedimentation rate for acid nickel effluent for varying coagulant dosages.

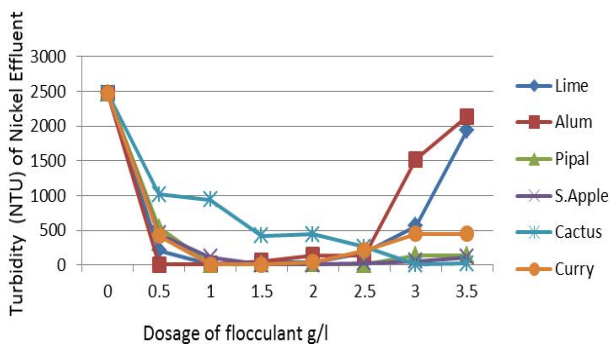


Fig. 4. Removal of turbidity for the treated nickel effluent.

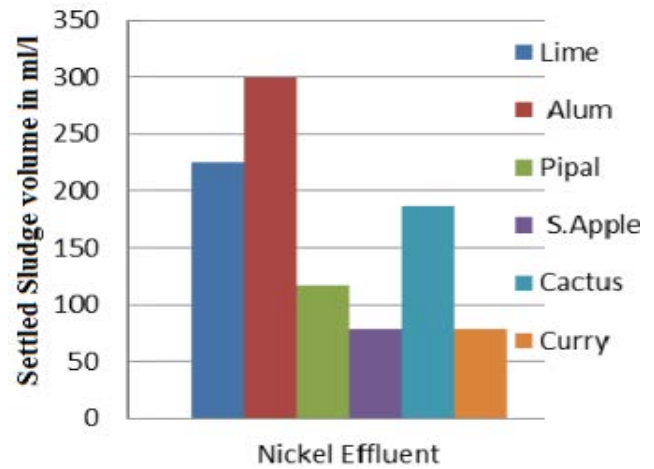


Fig. 5. Settled sludge volume for nickel effluent.

alum treatment is found to be 300 mL/L, with lime and biomass extracts such as pipal = 117 mL/L, S. Apple = 78 mL/L, cactus = 187 mL/L and for curry = 78 mL/L. From the SSV obtained for all the coagulants, we can conclude that the settled sludge volume is appreciably lower for the effluent samples treated with the biomass extracts compared to that produced by the treatment with lime and alum. Hence, it can be concluded that the biomass addition has a good control over the sludge volume compared to the lime alum combination.

3.3.5. BBD analysis

The BBD matrix for coded and actual values for pH, dosage of flocculants, and concentration of nickel are provided in Table 7. Results of BBD and its output for C/F with the biomass *A. squamosa* using Minneapolis for optimization is provided in Table 2.

The analysis of variance (ANOVA) or the regression models with the *F*-values showing the factors contributing to the C/F process in the sedimentation of acid nickel effluent, percentage removal of Ni(II) ions and turbidity of the treated effluent are summarized in Tables 8–10.

The insignificant lack of fit of 0.0688 (ANOVA 1), 0.1497 (ANOVA 2), and 0.0001 (ANOVA 3) for the quadratic model are validated for the current study. The non-significant lack of fit establishes the fitness of the model data. For the rate of sedimentation, the predicted r^2 (0.9845) and adjusted r^2 (0.997309) are closer to 1. Fig. 6 shows the predicted values are well-aligned with the actual values.

On similar lines, the removal percentage of Ni(II), the predicted r^2 (0.9917) and adjusted r^2 (0.9983), alignment of values are represented in Fig. 7. For turbidity, the predicted r^2 (0.9493) and adjusted r^2 (0.9642) and the fitness are shown in Fig. 8. The proposed models are validated by obtaining the quadratic equation for the three response variables 1, 2, and 3 as given below:

$$\begin{aligned} \text{Sedimentation} = & 0.924 + 0.0725 A - 0.06 B - 0.0125 C - \\ & 0.14 AB - 0.005 AC + 0.01 BC - 0.3345 A^2 - \\ & 0.3445 B^2 - 0.4595 C^2 \end{aligned} \tag{3}$$

Table 7
BBD matrix for coded and actual values for pH, dosage of flocculants, and concentration of nickel

Design summary							
Study type				Response surface			
Initial design				Box–Behnken			
Design model				Quadratic			
Runs				17			
Blocks				No blocks			
Factor	Name	Low		High		Mean	Standard deviation
		Coded	Actual	Coded	Actual		
A	pH	–1	7	1	9	8	0.685994
B	Dosage of flocculants	–1	0	1	1	0.5	0.342997
C	Conc. of nickel	–1	200	1	1700	950	514.4958

Table 8
ANOVA-1 results of sedimentation

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	2.222827	9	0.246981	659.8723	<0.0001	Significant
A-pH	0.04205	1	0.04205	112.3473	<0.0001	
B-Dosage of flocculant	0.0288	1	0.0288	76.94656	<0.0001	
C-Concentration of Ni.	0.00125	1	0.00125	3.339695	0.1104	
AB	0.0784	1	0.0784	209.4656	<0.0001	
AC	0.0001	1	0.0001	0.267176	0.6212	
BC	0.0004	1	0.0004	1.068702	0.3356	
A ²	0.471117	1	0.471117	1258.709	<0.0001	
B ²	0.499706	1	0.499706	1335.093	<0.0001	
C ²	0.889012	1	0.889012	2375.222	<0.0001	
Residual	0.00262	7	0.000374			
Lack of fit	0.0021	3	0.0007	5.384615	0.0688	Not significant
Pure error	0.00052	4	0.00013			
Cor total	2.225447	16				

Table 9
ANOVA-2 results of Ni(II) removal percentage

Source	Sum of squares	df	Mean square	F-value	p-value prob > F	
Model	9,623.397	9	1,069.266	1,103.067	<0.0001	significant
A-pH	68.445	1	68.445	70.60865	<0.0001	
B-Dosage of flocculant	9.90125	1	9.90125	10.21424	0.0152	
C-Concentration of Ni.	20.16125	1	20.16125	20.79858	0.0026	
AB	529	1	529	545.7225	<0.0001	
AC	1.96	1	1.96	2.021959	0.1980	
BC	235.6225	1	235.6225	243.0709	<0.0001	
A ²	1,679.582	1	1,679.582	1,732.676	<0.0001	
B ²	4,137.54	1	4,137.54	4,268.334	<0.0001	
C ²	2,065.313	1	2,065.313	2,130.6	<0.0001	
Residual	6.7855	7	0.969357			
Lack of fit	4.7575	3	1.585833	3.127876	0.1497	Not significant
Pure error	2.028	4	0.507			
Cor total	9,630.182	16				

Table 10
ANOVA-3 results of turbidity

Source	Sum of squares	df	Mean square	F-value	p-value Prob > F	
Model	25,135,309	9	2,792,812	48.86492	<0.0001	Significant
A-pH	1,740.5	1	1,740.5	0.030453	0.8664	
B-Dosage of flocculant	125,250.1	1	125,250.1	2.191461	0.1823	
C-Concentration of Ni.	57,291.13	1	57,291.13	1.002404	0.3501	
AB	1,831,962	1	1,831,962	32.05325	0.0008	
AC	200,256.3	1	200,256.3	3.503818	0.1034	
BC	10,816	1	10,816	0.189244	0.6766	
A ²	2,686,255	1	2,686,255	47.00053	0.0002	
B ²	10,832,774	1	10,832,774	189.5375	<0.0001	
C ²	7,187,015	1	7,187,015	125.7489	<0.0001	
Residual	400,076	7	57,153.72			
Lack of fit	400,067.3	3	133,355.8	60,699.02	<0.0001	Not significant
Pure error	8.788	4	2.197			
Cor total	25,535,385	16				

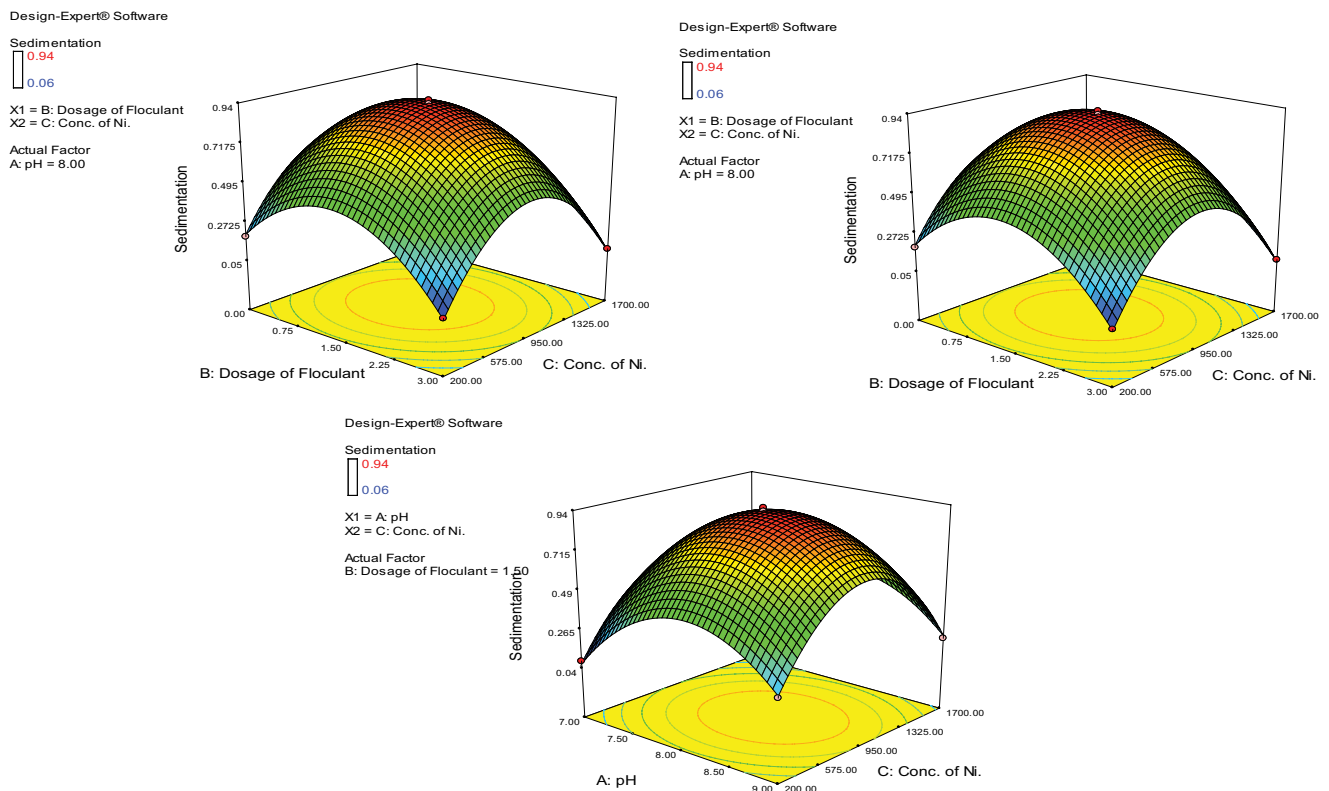


Fig. 6. Effect of pH, dosage of flocculant, and concentration of nickel in sedimentation.

$$\begin{aligned}
 \text{Ni(II) Removal \%} = & 90.22 + 2.925 A + 1.1125 B + \\
 & 1.5875 C - 11.5 AB - 0.7 AC - 7.675 BC - \\
 & 19.9725 A^2 - 31.3475 B^2 - 22.1475 C^2
 \end{aligned}
 \tag{4}$$

$$\begin{aligned}
 \text{Turbidity} = & 62.52 - 14.75 A - 125.125 B + 84.625 C + \\
 & 676.75 AB + 223.75 AC + 52 BC + 798.74 A^2 + \\
 & 1,603.99 B^2 + 1,306.49 C^2
 \end{aligned}
 \tag{5}$$

The Y-axis pH, dosage of flocculant, concentration of Ni ions are the significant parameters, indicating the importance of these variables in the C/F process using the biomass extracts. The ANOVA results provided in Tables 8–10 reveals that the reliability of the model is exceedingly significant due to the F-values with low probability ($p < 0.0001$).

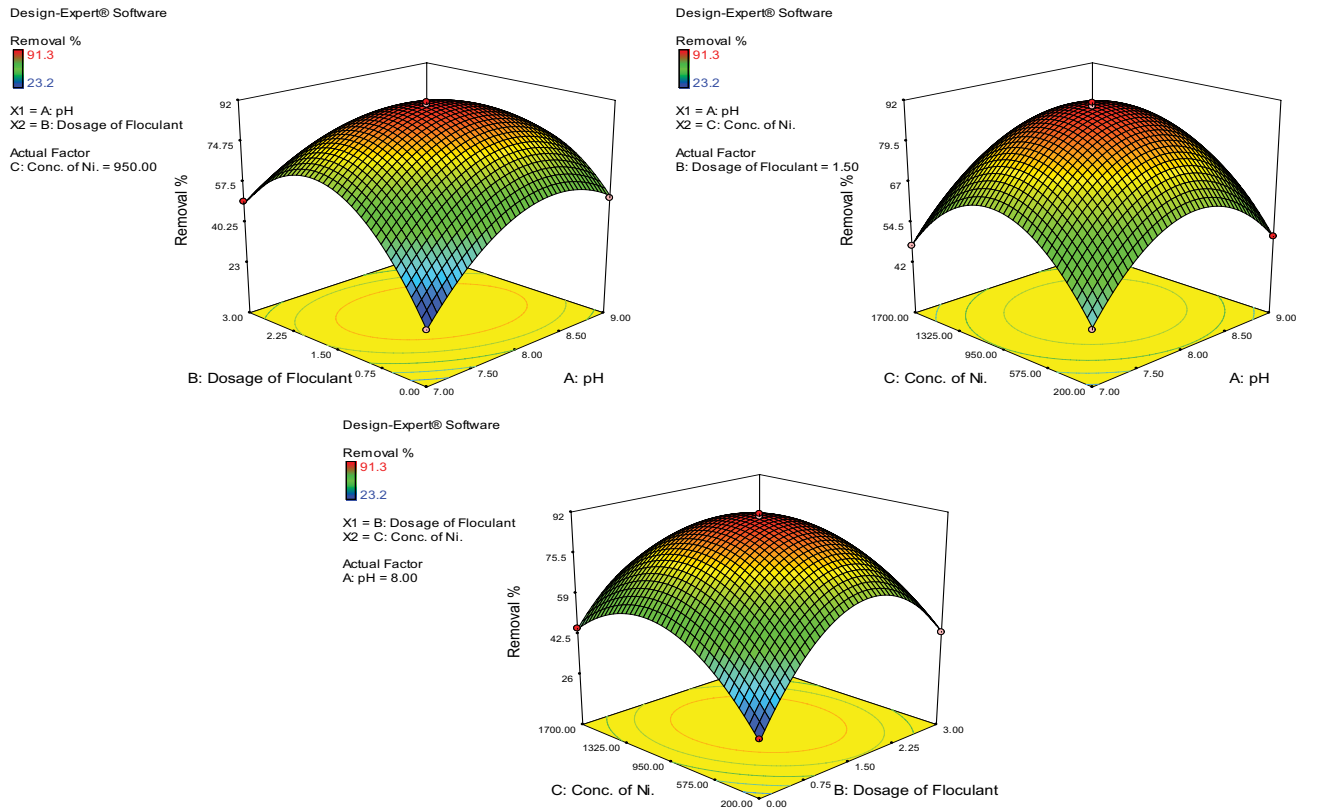


Fig. 7. Effect of pH, dosage of flocculant, and concentration of nickel in Ni(II) removal percentage.

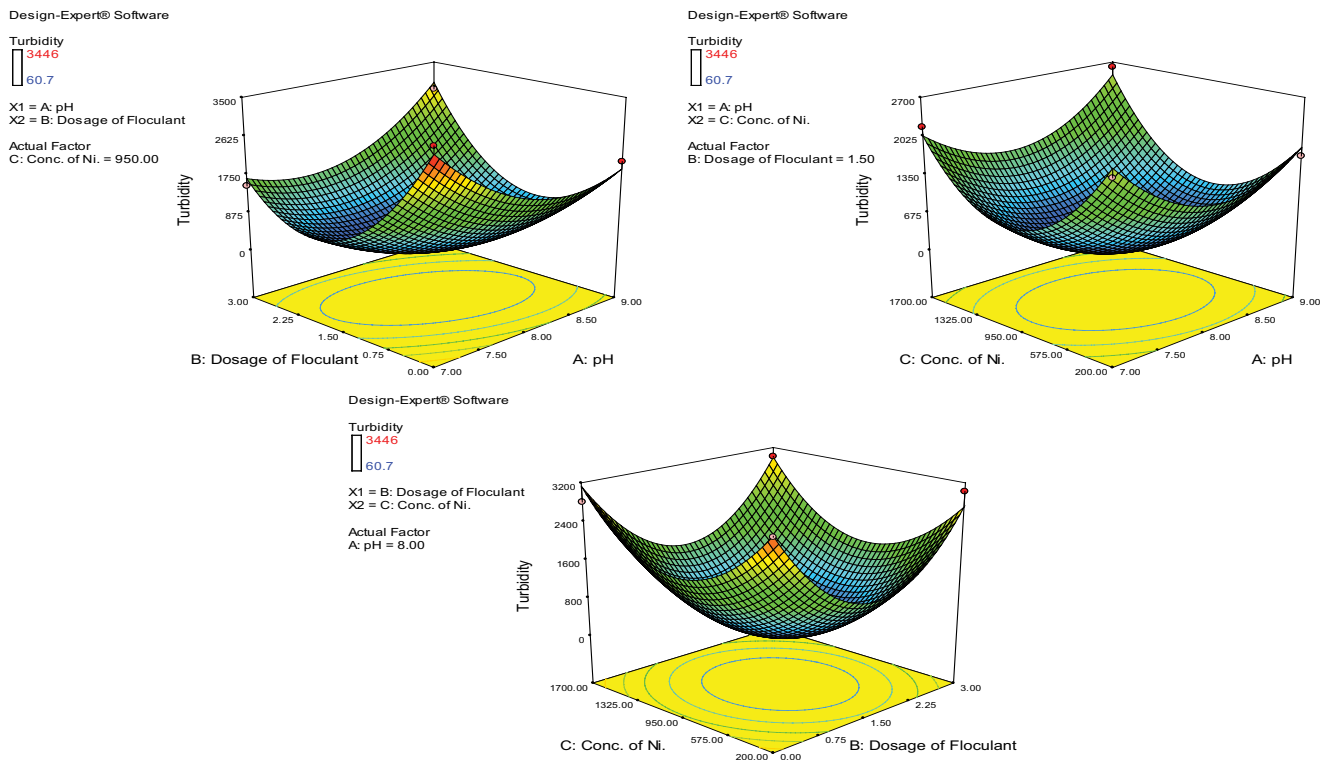


Fig. 8. Effect of pH, dosage of flocculant, and concentration of nickel in removal of Turbidity.

4. Conclusion

In this study, lime and alum, the time tested coagulant combination is replaced with lime-biomass extracts for the treatment of the nickel electroplating effluent. The addition of biomass extracts along with lime has proved to be very effective for the coagulation–flocculation process. Generally, long chain polymers or polyelectrolytes, which are capable of providing mechanical bridging, are added along with lime-alum combination for good flocculation. Here, the biomass extract, which are organic polymeric materials, when used along with lime additionally take up the role of a flocculant. Thus, the need for the usage of synthetic polyelectrolytes, which are usually added along with alum, has been eliminated and about 95% removal of the Ni(II) ions from the untreated effluent, when the initial metal ion concentration is less than 1,000 ppm, has been achieved. This however, has been found to be less efficient at much higher concentrations. Further studies in this direction, based on the utilization of biomass as an alum substituent for very high concentrations of metal ions in the effluent will enable us to develop an efficient treatment method for other metal ions and much higher metal ion concentrations as well.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. There is no conflict of interest for this manuscript.

Credit author statement

To whom it may concerns, all authors have seen and approved the final version of the manuscript being submitted. They warrant that the article is the authors' original work, hasn't received prior publication and isn't under consideration for publication elsewhere.

References

- [1] T.A. Kuriawan, G.Y.S. Chan, W.-H. Lo, S. Babel, Physico-chemical treatment techniques of wastewater laden with heavy metals, *Chem. Eng. J.*, 118 (2006) 83–98.
- [2] N. Adhoum, L. Monser, N. Bellakhal, J.E. Belgaid, Treatment of electroplating wastewater containing Cu²⁺, Zn²⁺ and Cr(VI) by electrocoagulation, *J. Hazard. Mater.*, 112 (2004) 207–213.
- [3] D.I. Barra-Rodriguez, J. Lizardi-Mendoza, E.A. Lopez-Maldonado, M.T. Oropeza-Guzman, Capacity of 'nopal' pectin as a dual coagulant-flocculant agent for heavy metals removal, *Chem. Eng. J.*, 323 (2017) 19–28.
- [4] C.Y. Yin, Emerging usage of plant-based coagulants for water and wastewater treatment, *Process Biochem.*, 45 (2010) 1437–1444.
- [5] V.M. Jadhav, S.Y. Mahajan, Assessment of feasibility of natural coagulants in turbidity removal and modeling of coagulation process, *Desal. Water Treat.*, 52 (2014) 5812–5821.
- [6] M.A. Martin-Lara, G. Blazquez, M.C. Trujillo, A. Perez, M. Calero, New treatment of real electroplating wastewater containing heavy metal ions by adsorption onto olive stone, *J. Cleaner Prod.*, 81 (2014) 120–129.
- [7] S. Vilvanathan, S. Shanthakumar, Removal of Ni(II) and Co(II) ions from aqueous solution using teak (*Tectona grandis*) leaves powder: adsorption kinetics, equilibrium and thermodynamics study, *Desal. Water Treat.*, 57 (2016) 3995–4007.
- [8] L.T. Adewoye, S.I. Mustapha, A.G. Adeniyi, J.O. Tijani, M.A. Amoloye, L.J. Ayinde, Optimization of nickel(II) and chromium(III) removal from contaminated water using *Sorghum bicolor*, *Nigerian J. Technol.*, 36 (2017) 960–972.
- [9] M. Saleem, N. Wongrisujarit, S. Boonyarattanakalin, Removal of Ni(II) ion by adsorption on coconut cobra meal biosorbent, *Desal. Water Treat.*, 57 (2016) 5623–5635.
- [10] A. Kurniawan, A.N. Kosasih, J. Febrianto, Y.H. Ju, J. Sunarso, N. Indraswati, S. Ismadji, Evaluation of cassava peel waste as low cost bio-adsorbent for Ni sorption: equilibrium, kinetics, thermodynamics and mechanism, *Chem. Eng. J.*, 172 (2011) 158–166.
- [11] K. Vijayaraghavan, K. Palanivelu, M. Velan, Crab shell-based biosorption technology for the treatment of nickel – bearing electroplating industrial effluents, *J. Hazard. Mater.*, 119 (2005) 251–254.
- [12] M.Z. Aslam, N. Ramzan, S. Naveed, N. Feroze, Ni(II) Removal by biosorption using *Ficus religiosa* (peepal leaves), *J. Chil. Chem. Soc.*, 55 (2010) 81–84.
- [13] T.L. Marques, V.N. Alves, L.M. Coelho, N.M. Coelho, Removal of Ni(II) from aqueous solution using *Moringa oleifera* seeds as a biosorbent, *Water Sci. Technol.*, 65 (2012) 1435–1440.
- [14] T. Nharingo, M. Moyo, Application of *Opuntia ficus-indica* in bioremediation of wastewater: a critical review, *J. Environ. Manage.*, 166 (2016) 55–72.
- [15] S. Vishali, R. Karthikeyan, *Cactus opuntia* (ficus-indica): an eco-friendly alternative coagulant in the treatment of paint effluent, *Desal. Water Treat.*, 56 (2015) 1489–1497.
- [16] G.H. Sonawane, V.S. Shrivastava, Orange-II removal from simulated wastewater by adsorption using *Annona squamosa* shell – a kinetic and equilibrium studies, *Desal. Water Treat.*, 36 (2011) 374–382.
- [17] C.P. Jebadass Isaac, A. Sivakumar, Removal of lead and cadmium ions from water using *Annona squamosa* I shell: kinetic and equilibrium studies, *Desal. Water Treat.*, 51 (2013) 7700–7709.
- [18] S. Qaiser, A.R. Saleemi, M. Umar, Biosorption of lead from aqueous solution by *Ficus religiosa* leaves: batch and column study, *J. Hazard. Mater.*, 166 (2009) 998–1005.
- [19] C.P. Devatha, A.K. Thalla, Y.K. Shweta, Green synthesis of iron nanoparticles using different leaf extracts for treatment of domestic waste water, *J. Cleaner Prod.*, 139 (2016) 1425–1435.
- [20] L.D. Benfield, J.M. Morgan, *Chemical Precipitation*, R.D. Letterman, Ed., *Water Quality and Treatment*, Mc Graw Hill, Inc., New York, NY, 1999, pp 10.1–10.57.
- [21] O. Tunay, Developments in the application of chemical technologies to wastewater treatment, *Water Sci. Technol.*, 48 (2004) 43–52.
- [22] I. Anastopoulos, A. Robalds, H.N. Tran, D. Mitrogiannis, D.A. Giannakoudakis, A. Hosseini-Bandegharai, G.L. Dotto., Removal of heavy metals by leaves derived biosorbents, *Environ. Chem. Lett.*, 17 (2019) 755–766.
- [23] M.A. Quraisi, A. Singh, V. Kumar Singh, D.K. Yadav, A. Kumar Singh, Green approach for corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves, *Mater. Chem. Phys.*, 122 (2010) 114–122.
- [24] R. Wangsagonup, S. Shobngob, B. Oonkhanond, S. Varavinit, Zeta Potential (ζ) Analysis for the determination of protein content in rice flour, *Starch*, 57 (2005) 25–31.
- [25] V.K. Gupta, I. Ali, T.A. Saleh, A. Nayak, A. Shilpi, Chemical treatment technologies for waste water recycling – an overview, *RSC Adv.*, 2 (2012) 6380–6388.
- [26] A.K. Verma, R.R. Dash, P. Bhunia, A Review on chemical coagulation/ flocculation technologies for removal of colour from textile wastewater, *J. Environ. Manage.*, 93 (2012) 154–168.