

# Ultrasonic Preparation of Activated Carbon Composites for Removal of Cr<sup>3+</sup> and Zn<sup>2+</sup> Ions from Aqueous Solution

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## Abstract

In the present study melamine–formaldehyde-tetraoxalyl-ethylene diamine (MFT) covered activated carbon (MFT/AC) was prepared by the use of ultrasonic waves. The prepared materials were examined by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The results showed that MFT was symmetrically covered the surface of the activated carbon. MFT/AC was examined for the removal of chromium and zinc ions from their aqueous solution in the presence and absence of ultrasonic waves. The effects of initial pH of the heavy metal solution, ultrasonic time and ultrasonic frequency on the efficiency of the removal were studied. The results showed that, using ultrasonic waves of 210 KHz for sonication time 30 minutes showed higher removal efficiency towards Cr<sup>3+</sup> and Zn<sup>2+</sup> ions than unsonicated treatment. The removal of Cr<sup>3+</sup> ions was higher than that of Zn<sup>2+</sup> ions. The removal process was done via chelating with MFT in the prepared carbon composite.

**Keywords:** Ultrasonic waves; Carbon composites; Chelation; Cr<sup>3+</sup> and Zn<sup>2+</sup> ions

## Introduction

Heavy metals and other toxic pollutants are considered extremely pernicious because they are toxic, non-degradable, and environmentally persistent. Electroplating, metal finishing, and/or leather tanning produce waste water streams contaminated with heavy metals such as chromium, zinc, cadmium, lead, nickel, and mercury [1]. Pollution by heavy metals ions due to intense industrial activity results in the accumulation of these toxic effluents in biosphere especially water sources. From those toxic heavy metals zinc and chromium ion. The extensive use of chromium and zinc in industry means that considerable amounts of these metals can find their way into the aquatic environment. Chromium is employed in several industrial activities, including mineral processing, electroplating, production of paint sand batteries, manufacturing of sulphate and porcelain enameling [2-4]. Zinc is released into the aquatic environment through several industrial activities, such as mining, metal coating, battery production and its use in paints, ceramics, wood, fabrics, drugs, sun block sand deodorants [5-7]. Human exposure to these heavy metals at significant levels is associated with serious health effects. Chromium is associated with dermatitis, nausea, coughing, chronic bronchitis, gastrointestinal distress, reduced lung function and lung cancer [8-10]. Among various treatment methods such as alkaline precipitation ion exchange, solvent extraction [11], electrodialysis [12], electrolytes [13] and removal by activated carbon [14]. Carbon could be activated by several methods including acid or base treatment, salt treatment, use of microwaves and ultrasonic waves.

Ultrasound is a wave of frequency  $2 \times 10^4$  to  $10^{10}$  Hz. When ultrasonic wave passes through a liquid medium, a large number of micro bubbles form, grow, and collapse in a very short time about a few microseconds, which is called ultrasonic cavitations [15]. The cavitations can generate local temperatures as high as 5,000 K and local pressures as high as 500 atm, with heating and cooling rates greater than  $10^9$  K/s, a very vigorous environment which can break the molecules existed in the medium to produce free radical to initiate monomer polymerization [16,17]. Compared to conventional chemical

reaction, no chemical initiators are used in the ultrasonic polymerization, which can produce faster polymerization, higher monomer conversion and molecular weight with economical expense. On the other hand, because ultrasonic degradation technology has significant advantages in terms of safety, cleanliness, energy conservation and without secondary pollution [18], an increasing concentration also into wastewater treatment [19-21]. The present work focused on the investigation of using prepared active carbon composite which covered with chelating resin. These composites used in the removal of Cr<sup>3+</sup> and Zn<sup>2+</sup> ions from their aqueous solutions with the aid of ultrasonic waves. Effects of initial pH of the solution, sonication time and frequency on the removal process were studied.

## Experimental

### Materials

Rice husk (Sigma-Aldrich) was used as a source of activated carbon. All chemicals used in this study were of analytically reagent grade, commercially available from fulka and used without previous purification. Heavy metals solutions were prepared using distilled water. Adjustment of solution pH to the desired value was achieved using 0.1M NaOH and HCl.

### Methods

**Preparation of activated carbon (AC):** First rice husk was washed and dried in oven at 110°C, then it heated in a furnace at 400°C for 2 hours. The prepared carbon was activated as follow: 3 gm of carbon was

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dispersed in 10 mL of mixed acid solution of nitric acid and sulfuric acid (7:3), then the mixture was ultrasonically agitated for 6 hrs, this was done by using Ultrasonic Processing Shanghai Shengxi Ultrasonic instrument Co. Ltd) at 210 kHz of intensity 7.7 W/cm. The resulted activated carbon (AC) was washed with doubly distilled water to neutral pH, and dried in a vacuum at 100°C for 12 hr.

### Preparation of (MFT/AC)

Melamine-formaldehyde-tetraoxalyl-ethylenediamine chelating resin modified active carbon (MFT/AC) was prepared as follow [22]. 5 gm of AC was immersed in a 5 mmol/L of ethylene diamine for 5 hrs, the mixture was ultrasonically agitated for 30 min under a flow of N<sub>2</sub> to form amine-AC. 5 gm of amine-AC was immersed in a solution including 1.5 g tetraoxalyl ethylenediamine and 1.8 g melamine, 20 mL 15% formaldehyde and 0.1 g sodium dodecyl sulfate with 4 hr immersion. After immersion the solution was sonicated at acoustic intensity of 7.7 W/cm, 210 KHz for one hour and the pH was adjusted at 2.5. It Then filtration was carried out and the precipitation was washes with ethanol and dried in vacuum for 12 hrs, the prepared MFT/AC was characterized by FTIR and SEM.

### Apparatus

**SEM and FTIR:** Scanning electron microscope (SEM) was carried out to investigate the morphology and the particle size of prepared active carbon and the activated carbon composites. This was carried out by using a JEOL (JEM 2010) scanning electron microscope. The FTIR spectra of MFT/AC and MFT/AC loaded by Cr<sup>3+</sup>, Zn<sup>2+</sup> ions were obtained using a Fourier transform infrared spectrometer (BIO-RAD FTS-40).

### Removal process

MFT/AC was used in the removal of Cr<sup>3+</sup> and Zn<sup>2+</sup> ions from their aqueous solution. This was done with the aid of ultrasonic waves. Sonication experiments were carried out by introducing 0.05 g of MFT/AC in a series of beakers containing 50 mL of heavy metal solutions of initial concentration 100 mg/L at 25°C. The effect of initial pH of the heavy metal solution (from 3-9), ultrasonic time (0-60 minutes), and ultrasonic frequency (210, 300 and 516 kHz) on the efficiency of the removal were studied. The desired pH was controlled using HCl and NaOH solutions, and measured using pH meter (Orion Research Inc.). At the end of the each experiment, filtration was carried out and the remaining concentration of each heavy metal ions in the filtrate was determined using atomic absorption spectroscopy (AAS) using a Perkin-Elmer, PE 703 instrument. The condition of the measurement was summarized in Table 1. The removal efficiency (Q) was calculated using the following equation:

$$Q\% = \frac{C_i - C_f}{C_f} \times 100$$

Where: Q is the of the removal coefficient, C<sub>i</sub> and C<sub>f</sub> are the concentrations of the heavy metal ion in solution before and after removing process (mg/L).

## Results and Discussion

### SEM

A scanning electron microscope was used to look at the effect of ultrasound on the morphology of the carbon surface. Figure 1a showed SEM micrographs of carbon derived from rice husk after heating for 400°C. Here a homogeneous amorphous particle can be detected. After

Zn <sup>2+</sup>	Cr <sup>3+</sup>	Conditions
320	298	Wavelength, nm
10	10	Lamp current, mA
1.3	1.3	Slit width
80-120	80-120	Heating program Drying temp., °C
30	30	Time/sec
400	300	Ashing temp., °C
30	30	Time/sec
2100	1700	Atomization temp., °C
7	7	Time/sec
3000	2600	Cleaning temp., °C
30	30	Time/sec

Table 1: Operational conditions for AAS measurement.

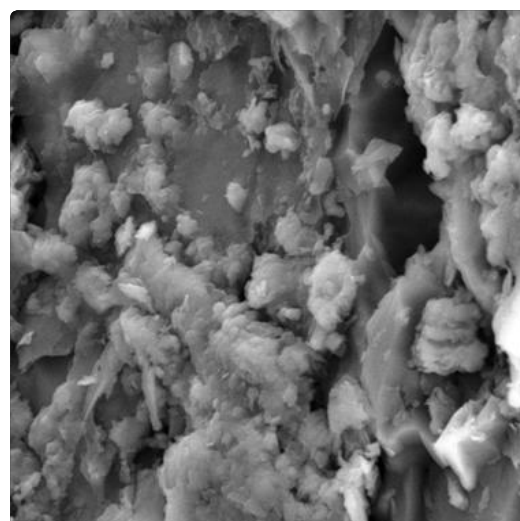


Figure 1a: SEM of carbon.

acid followed by ultrasonic waves treatments, dramatic effects occurred on the solid surface which is responsible for pitting and fracturing erosion of the surface. When ultrasound waves are introduced into an aqueous solution, cavitations occurs due to bubbles formation and subsequently collapse inward from the build-up of pressure through rarefaction/compression cycles. Under these conditions, high temperatures and pressures accompany the implosion of cavitations. These cavitations acts as active sites on which chelation can occurred, (Figure 1b).

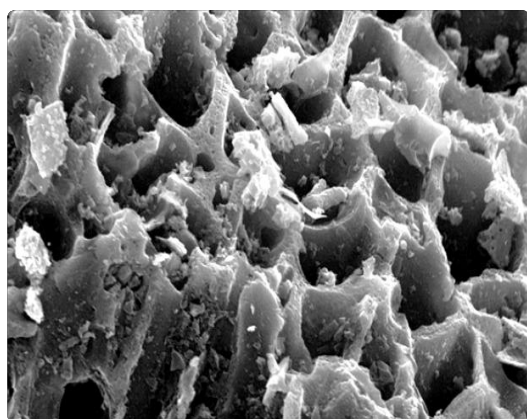
Figure 1c showed MFT/AC, here the activated carbon treated with MFT chelating agent. A layer of MFT resin covered the inner and outer surfaces and cavities of activated carbon can be seen in SEM micrographs. Under the preparing conditions, MFT could be polymerized [22]. Since tetraoxalyl ethylene diamine molecule in the MFT chelating agent has EDTA-like (Ethylene diamine tetra-acetic acid) structure, it was expected that it could form stable complexes with metal ions.

### FTIR

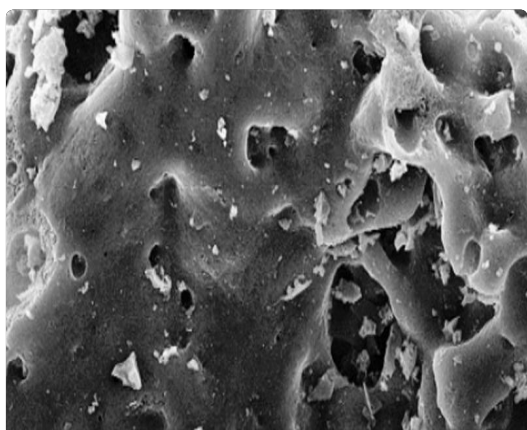
Table 2 showed the analysis of FTIR spectra of unloaded MFT/AC and Cr<sup>3+</sup>, Zn-loaded MFT/AC. Here FTIR were taken to obtain information on the nature of possible interactions between the functional groups of MFT/AC and the metal ions during the removal process. The FTIR spectrum of MFT/AC showed a broad band at 3409 cm<sup>-1</sup> may be

MFT/NC	MFT/NC-Cr	MFT/NC-Zn	Assignment
3409	3421	3408	-OH and -NH <sub>2</sub> stretching
2921,2855	-	2921,2855	-CH symmetric stretching of aliphatic groups
1651	1641	1649	-C=O asymmetric stretching
1447	1441	1447	- C=O symmetric stretching
1230	1245	1240	-Carboxyl group symmetric stretching
1078	1065	1078	-CO stretching of alcoholic group.
-	617	-	- NH-Cr stretching band

**Table 2:** FTIR bands in AC and M FT/AC.



**Figure 1b:** SEM of activated carbon.



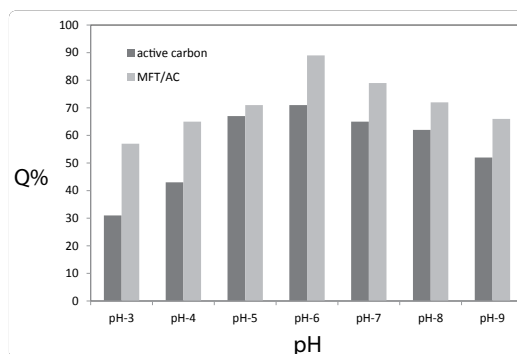
**Figure 1c:** SEM of activated carbon.

due to the overlapping of O-H and -NH<sub>2</sub> stretching vibration. This band shifted to 3421 cm<sup>-1</sup> and its intensity decreased after chromium removal indicating the interaction between these functional groups and the removed ion. Two bands at 2921 and 2855cm<sup>-1</sup> are observed in MFT/AC which is assigned to the -CH stretching of the CHO group. These two bands nearly disappeared after chromium binding and lowered after Zn<sup>2+</sup> binding. A strong asymmetric C=O stretch (aldehydes or/ and carboxylic groups) initially present at 1651 cm<sup>-1</sup>. Such band was shifted to 1641 cm<sup>-1</sup> after chromium ion removal and its intensity decreased indicating changes in carboxyl symmetry after chromium

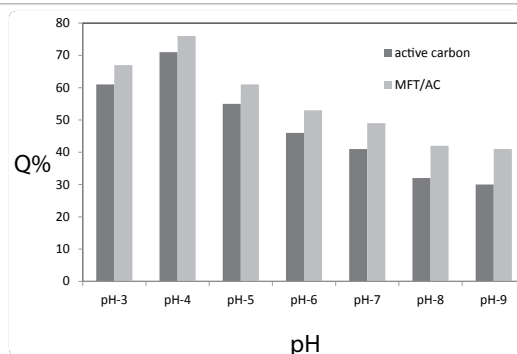
binding. Such shift was lower in case of Zn<sup>2+</sup> ion which attributed to the weak interaction of Zn<sup>2+</sup> ions with MFT/AC compared to chromium ions. Another band was observed in MFT/AC at 1447 cm<sup>-1</sup> may be attributed to symmetric stretching vibration of C=O groups and was shifted to 1441 cm<sup>-1</sup> after Cr(III) binding. This decrease, coupled with a peak increase of the C-O stretch from 1230 to 1245 cm<sup>-1</sup> after binding pointed to possible chelating between carboxyl groups in MFT/AC and chromium ions. Moreover, a new band at 617 cm<sup>-1</sup> could be observed in MFT/AC-Cr, which probably attributed to coordination bonding between chromium ions and amino groups in the chelating agent [22]. Such finding agrees with Jin et al. which showed the heavy metal linked to MFT/AC through chelating adsorption [23].

### Removal of Cr<sup>3+</sup> and Zn<sup>2+</sup> ions

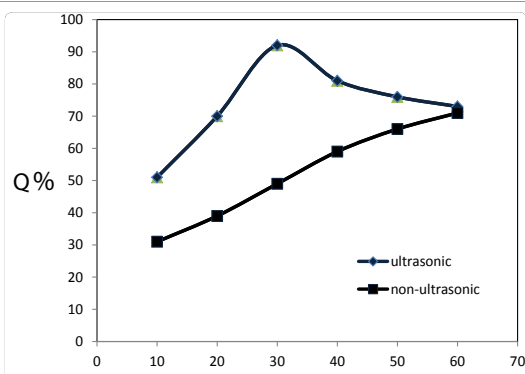
**Effect of initial pH:** The influence of initial pH on the removal efficiency for Zn<sup>2+</sup> and Cr<sup>3+</sup> ions was studied in a range of pH (3-9) and represented in (Figures 2a and 2b). This was done by soaking 0.05 g of MFT/AC or AC in a beaker containing 50 mL of heavy metal solutions of initial concentration 100 mg/L at 25°C and the mixture was sonicated at 210 KHz, at acoustic intensity of 7.7 W/cm for 1 hrs. As shown in (Figure 2), Metal ions removal from aqueous solution into MFT/AC was a pH dependent process due to pH influence on both the chemistry of metal ions and MFT functional groups. The removal coefficient of MFT/AC was greater than those of activated carbon at all pH ranges. For chromium ions, the removal coefficient towards Cr<sup>3+</sup> ions was increasing from pH 3 to 6, it reached a maximum at pH 6. About 91% of chromium ions are removed from solution at pH=6. In pH range (7-9) the removal coefficient slightly decreased. For Zinc ions, the removal coefficient reached maximum at pH 4, 74% of zinc ions are removed



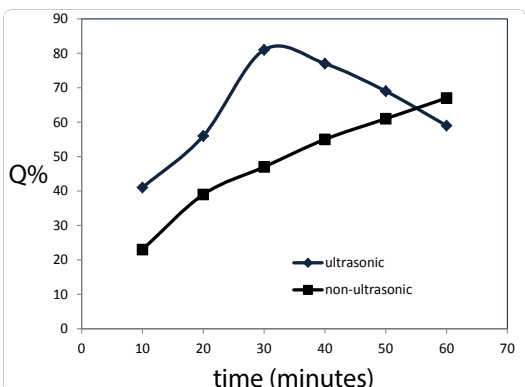
**Figure 2a:** Percentage of removal efficiency (Q%) of activated carbon and MFT/AC composite at various pH solution Cr<sup>3+</sup> ions.



**Figure 2b:** Percentage of removal efficiency (Q%) of activated carbon and MFT/AC composite at various pH solution Zn<sup>2+</sup> ions.



**Figure 3a:** Percentage of removal efficiency (Q%) in presence and absence of ultrasonic waves at different removal times Cr ions.



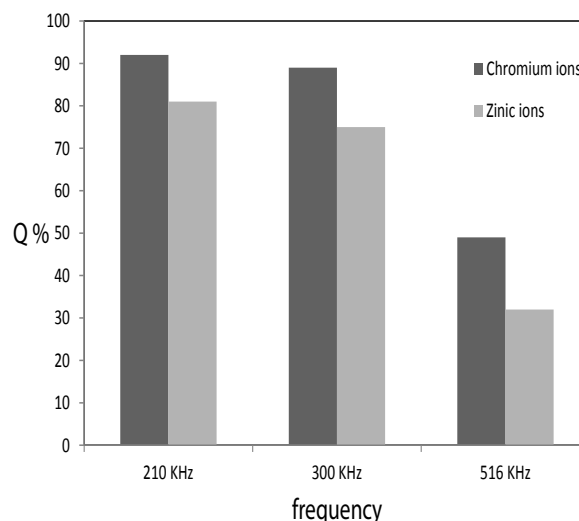
**Figure 3b:** Percentage of removal efficiency (Q%) in presence and absence of ultrasonic waves at different removal times Zn ions.

here, then it obviously decreased. In neutral or slightly acidic media, the uptake probably attributed to the stable formation of resin-metal ion complex, which could cause increase of the acidity of the medium due to release of H<sup>+</sup> from coordinating carboxylate groups [24]. At higher pH values, heavy metal ions will hydrolysis to become Cr(OH)<sup>+</sup> and Zn (OH)<sup>+</sup> [25] and as consequence, the heavy metal positive charge was reduced to +1 which make low interaction with the chelating agent besides metal hydroxides could be precipitates.

**Effect of sonication time and frequency:** Ultrasonic waves can be used to enhance the possible complexation between the chelating agent (MFT) and the heavy metal ions due to temperature and pressure effects. To showed these effects and determine the best sonication time and frequency for the removal process, the following experiments are rried out.

The effect of sonication time on the removal efficiency of Zn<sup>2+</sup> and Cr<sup>3+</sup> ions was carried out by immersing 0.05 gm MFT/AC with 50 mL of Cr<sup>3+</sup> and Zn<sup>2+</sup> solutions (100 mg/L) in presence and absence of ultrasonic waves of frequency 210 kHz, at acoustic intensity of 7.7 W/cm. The results are shown in (Figures 3a and 3b).

In the absence of ultrasonic waves the removal coefficient of MFT/AC toward both the two heavy metals increased continuously with the removal time and about 71% of Cr ion and 60% of Zn ions are removed after 60 minutes of the removing process. When the ultrasonic waved used in the removal process, for both two heavy, the removal coefficient increased with increasing the sonication period in the range 0-30



**Figure 4:** Removal efficiency at various ultrasonic frequencies.

minutes to become 92% for chromium ions and 81% for zinc ions, see (Figures 3a and 3b). In sonication period (40-60 minutes), the removal coefficient greatly to became equal to that obtained in non-sonicated solutions (for chromium) and lower than those obtained in non-sonicated solutions (for zinc). At earlier sonication period, and under the aid of pressure relief-dipping-ultrasonic waves, the coordination of MFT with the heavy metal enhanced. While as later sonication period (from 30-60 minutes) and due to dramatic effect of ultrasonic waves, high pressure and temperature generated in the solutions could decrease the particle size of MFT. This decreases the possible chelation and breaking of the already formed chelating bonds between the metal ion and MFT which is responsible for decreasing the removal of the heavy metal ions [25].

Effect of the ultrasonic frequency on the removal efficiency of chromium and zinc ions was carried by immersing 0.05 gm of MFT/AC with 50 of Cr<sup>3+</sup> and Zn<sup>2+</sup> ions and sonicated for 30 minutes using ultrasonic waves of 210, 300 and 516 kHz, at acoustic intensity of 7.7 W/cm. The results are shown in (Figure 4). Using ultrasonic waves with 210 300 KHz waves showed removal efficiency comparable to those obtained for 210 kHz while 516 KHz waves showed greatly low removal values. Increasing the sonication frequency increases its degradation power which decrease the possible chelation occurred between the heavy metal ions and MFT/AC. These explain why 210 and 300 kHz waves showed higher removal efficiency than 516 kHz waves.

## Conclusion

From the obtained results we can concluded that Using ultrasonic waves in the preparation of melamine-formaldehyde-tetraoxalyl-ethylene diamine covered activated carbon (MFT/AC) enhances its ability for removing chromium and zinc ions from their aqueous solution. According to results of SEM and FTIR, MFT was symmetrically covered the surface of the activated carbon forming an active centers for chelating metal ions. Ultrasonic waved was used as fast and effective techniques for the removing of chromium and zinc ions from aqueous solution. The results showed that, using ultrasonic waves of 210 KHz for sonication time for 30 minutes dives high removal efficiency towards Cr<sup>3+</sup> and Zn<sup>2+</sup> ions. These attributed to the possible chelation between the chelating agent (MFT) on the surface of MFT/AC and the heavy metal ions.



## References

- Weng CH, Huang CP (1994) Treatment of Metal Industrial Wastewater by Fly Ash and Cement Fixation. J Environmental Engineering 120: 1470-1487.
- Beliles RP (1978) The lesser metals. In: Oehme FW (ed). Toxicity of Heavy Metals in the Environment Part 2. Marcel Dekker, New York. 547-616.
- Akhtar N, Iqbal J, Iqbal M (2004) Removal and recovery of nickel(II) from aqueous solution by loofa sponge-immobilized biomass of *Chlorella sorokiniana*: characterization studies. J Hazard Mater 108: 85-94.
- Farooq U, Kozinski JA, Khan MA, Athar M (2010) Biosorption of heavy metal ions using wheat based biosorbents - a review of the recent literature, Bioresour Technol 101: 5043-5053.
- Cheremisinoff PN (1995) Handbook of Water and Wastewater Treatment Technology. Marcel Dekker Inc, New York.
- Zoumis T, Calmano W, Forstner U (2000) Demobilization of heavy metals from mine wastewaters. Acta Hydrochim Hydrobiol 28: 212-218.
- Dimirkou A (2007) Uptake of Zn<sup>2+</sup> ions by a fully iron-exchanged clinoptilolite. Case study of heavily contaminated drinking water samples. Water Res 41: 2763-2773.
- Kurniawan TA, Chan GYS, Lo WH, Babel S (2006) Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366: 409-426.
- Kurniawan TA, Chan GYS, Lo WH, Babel S (2006) Physico-chemical treatment techniques for wastewater laden with heavy metals. Chemical Engineering Journal 118: 83-98.
- Arief VO, Trilestari K, Sunarso J, Indraswati N, Ismadi S (2008) Recent progress on biosorption of heavy metals from liquids using low cost biosorbents: characterization, biosorption parameters and mechanism studies. Clean Soil Air Water 36: 937-962.
- Sana T, Shiomi K, Kawano Y (2005) Extraction rate of nickel with 5 dodecylsalicylaldehyde in a vibro-mixer. Sep Purif Technol 44: 160-165.
- Kuboi Y, Takeshita R (1989) Extension of bath life by electrodialysis method at electrodeless nickel plating baths. In: American EN 89 Conference. New York.
- Idhayachander R, Palanivelu K (2010) Electrolytic recovery of nickel from spent electrodeless nickel bath solution. E-Journal of Chemistry 7: 1412-1420.
- Madhavakrishnan S, Manickavasagam K, Rasappan K, Shabudeen PSS, Venkatesh R, et al. (2008) *Ricinus communis* pericarp activated carbon used as an adsorbent for the removal of Ni (II) from aqueous solution E-Journal of Chemistry 5: 761-769.
- Mason TJ, Lorimer JP (1988) Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry. Ellis Horwood, Chichester, UK.
- Yin N, Chen K, Kang W (2006) Preparation of BA/ST/AM nano particles by ultrasonic emulsifier-free emulsion polymerization. Ultrason Sonochem 13: 345-351.
- Ooi SK, Biggs S (2000) Ultrasonic initiation of polystyrene latex synthesis. Ultrason Sonochem 7: 125-133.
- Chowdhury P, Viraraghavan T (2009) Sonochemical degradation of chlorinated organic compounds, phenolic compounds and organic dyes-A review. Sci Total Environ 407: 2474-2492.
- Xie W, Qin Y, Liang D, Song D, He D. (2011) Degradation of m-xylene solution using ultrasonic irradiation. Ultrason Sonochem 18: 1077-1081.
- Xu LJ, Chu W, Graham N (2013) A systematic study of the degradation of dimethyl phthalate using a high-frequency ultrasonic process. Ultrason Sonochem 20: 892-899.
- Zhao JL, Wang XX, Zhang LB, Hou X, Li Y, et al. (2011) Degradation of methyl orange through synergistic effect of zirconia nanotubes and ultrasonic wave. J Hazard Mater 188: 231-234.
- Dragan ES, Dinu MV, Lisa G, Trochimczuk (2009) Study on metal complexes of chelating resins bearing iminodiacetate groups. European Polymer Journal 45: 2119-2130.
- Jin GP, ZhuXH, Li CY, Fu Y, Guan JX, et al. (2013) Tetraoxalyl ethylenediamine melamine resin functionalized coconut active charcoal for adsorptive removal of Ni (II), Pb (II) and Cd (II) from their aqueous solution. Journal of Environmental Chemical Engineering 1: 736-745.
- AE Vasu (2008) Surface Modification of Activated Carbon for Enhancement of Nickel (II) Adsorption. E - Journal of Chemistry 5: 814-819.
- Ghazy SE, El-Mosy SM (2009) The Sorption Of Lead From Aqueous Solution By Modified Activated Carbon Prepared From Olive Stones. African Journal of Biotechnology 8: 4140-4148.