
ULTRASOUND-ENHANCED COPPER REMOVAL BY HYDROUS IRON OXIDE ADSORPTION

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ABSTRACT A model system to investigate ultrasound-enhanced removal of metallic ions from aqueous solution by hydrous ferric oxide (HFO) adsorption has been conducted. The experimental data indicate that ultrasonic treatment of pre-formed HFO flocs can lead to enhanced removal of metallic ions from aqueous solution and that the level of enhancement is strongly correlated with the solution pH. Ultrasonic treatment has been shown to be effective at lowering the final solution concentration of copper species in the pH range 7.5-9.5 at copper to iron molar concentration ratios of 10 and 30%.

KEYWORDS: hydrous ferric oxide, iron III oxide, ultrasound, adsorption, heavy metals

INTRODUCTION

Benefaction of product streams and removal of contaminants from waste effluents with hydrous metal oxide (HMO) adsorbents is currently a standard form of industrial treatment. In fact, adsorption and/or coprecipitation of dissolved or suspended organic and inorganic material on and within HMO flocs followed by additional unit operations like coagulation, sedimentation, and rapid sand filtration is, in many instances, the preferred form of product stream and waste water treatment [1-2].

In general practice, industrial waste water containing inorganic and organic contaminants is frequently treated by a coprecipitation mechanism. Coprecipitation treatment steps include acidification of the incoming waste water to induce ionization, combination of the acidified influent with an acidic solution of HMO, and simultaneous precipitation of insoluble species via pH adjustment to the alkaline range. This procedure results in efficient removal of insoluble contaminants but carries a plethora of additional costs that could be avoided if

the adsorption capacity of a pre-formed adsorbent could be made equal to that obtained by coprecipitation. These added expenditures include, but are not limited to, the cost of acid necessary to preacidify the influent, the cost of the excess alkaline agent required to neutralize the added acid, the disposal and handling costs associated with the excess sludge created which include labor, operation, maintenance, and transportation expenditures, and a partially hidden long-term societal cost associated with depletion of available hazardous and non-hazardous landfill capacity.

One common HMO system utilized to remove dissolved and suspended contaminants is based on adsorption/coprecipitation of iron-based chemical coagulant aids (ex., $\text{Fe}(\text{Cl})_3$). The methodology involves treating the waste or product stream with iron salts followed by pH modification of the resulting solutions to values greater than approximately 3.0, leading to hydrolysis reactions and the subsequent formation of hydrous ferric oxide (HFO) as an amorphous adsorbent. This HFO is able to remove dissolved

contaminants through surface adsorption, coprecipitation, and through precipitate formation linked to subsequent sedimentation sweeping material from suspension (sweep flocculation).

From an economic point of view, HFO, which is frequently formed from the beneficial reuse of iron-containing waste liquors, has been successfully utilized to reduce the concentration of and enhance the recovery of hazardous contaminants and potentially valuable metallic elements (As, Se, Ni, Cu, Cr, and Zn) in a variety of waste streams [3-6]. Thus, the fundamental basis of HMO treatment is the low cost of the metal salts and neutralization agents used to form the adsorbing floc and the disposal cost savings derived from an operator's ability to modify the resultant sludge's characteristics to meet the non-hazardous waste landfill disposal requirements of the Environmental Protection Agency's Toxic Characteristic Leaching Procedure (TCLP).

ADSORPTION, COPRECIPITATION, AND SEQUESTRATION

Adsorption is the interphase transfer of material from a homogeneous or heterogeneous fluid matrix onto a solid surface. Coprecipitation describes a phenomenon where a "mixed" precipitate comprised of two or more insoluble species are simultaneously removed from solution. Sequestration, as defined below for an ultrasound irradiated system, differs in a fundamental way from simple adsorption and coprecipitation.

The findings of Kolthoff and Moskovitz [7], Crosby, *et al.* [8], Swallow, *et al.* [9], and Gadde and Laitinen [10] describing

adsorption phenomenon on HFO were of particular interest during the formulation of this project. The results of Kolthoff and Moskovitz [7] indicated that a small but measurable increase in cation (Cu^{2+}) removal could be induced by co-precipitating copper with iron instead of simply adsorbing the copper on the surface of the pre-formed HFO precipitate. Their explanation for this observation was that the HFO floc contained adsorption sites within its bulk matrix that were kinetically inaccessible to cations in solution but that these intra-floc adsorption sites were available during co-precipitation, i.e., when the cation (adsorbate) was present in solution as the adsorbent was formed. Crosby, *et al.* [8] also proposed a porous HFO structure and, on the basis of hysteresis observations, postulated that narrow-necked, wide-bodied pores appeared to predominate in iron (III) floc. A similar model of HFO floc as an open, permeable structure was proposed by Swallow, *et al.* [9] but these researchers found no removal difference for Cu^{2+} or Pb^{2+} when these metals were co-precipitated with iron or added after the iron precipitate had been formed in artificial seawater. Finally, the concept of an open porous structure for HFO was supported by the work of Gadde and Laitinen [10] who demonstrated enhanced removal of lead (Pb^{2+}) by coprecipitated HFO when compared with pre-formed HFO adsorbent, suggesting that available adsorption sites were kinetically inaccessible in the pre-formed floc. From this literature review it was apparent that many unanswered questions concerning the nature of the HMO adsorbent's structure remained. We therefore formulated a project based upon the use of ultrasound as a probe with which to interrogate the HMO adsorbent system.

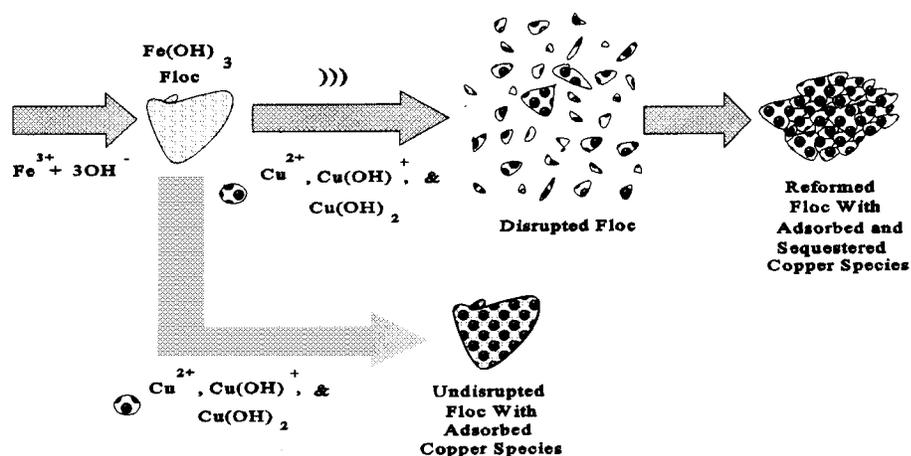


FIGURE 1. ULTRASONIC SEQUESTRATION AND UNSTIMULATED ADSORPTION.

Ultrasound

Ultrasonic radiation spans a range of frequencies from approximately 20 kilohertz (KHz) to 10 megahertz (MHz). Ultrasound exists in liquids as a flow of non-electromagnetic vibratory power per unit area or volume (energy intensity and energy density, respectively). Because of its physical character in aqueous solutions (i.e., wavelength ≈ 7.45 cm at a propagation velocity of approximately 1,500 meters/sec), ultrasonic radiation with a frequency of 20,000 Hz cannot act directly on adsorbed or soluble molecular species to induce chemical change [11-12]. Instead, at low intensities (less than approximately one watt/dm³), ultrasound acts to induce localized regions of enhanced flow (acoustic microstreaming) thereby altering the nature of diffusion processes in the proximity of solid interfaces [13-14]. At higher intensities ultrasonic fields are capable of inducing dramatic physical and chemical changes linked to acoustic cavitation [15-16]. For the most part the physical and chemical changes observed in heterogeneous systems exposed to intense ultrasound result from highly localized thermal and hydrodynamic forces that develop in and around collapsing

cavitation bubbles [17-18], although bulk circulation can also play a significant role in some systems [19].

Based on this literature review we anticipated that cavitation induced by intense ultrasound would be capable of disrupting an HFO floc and that this disruption should lead to enhanced uptake of metal species by the exposed adsorption sites of the porous floc. For our hypothetical model we have defined the kinetically inaccessible adsorption sites that become exposed during ultrasonic irradiation as the “internal adsorption capacity (IAC)” of the floc. In a similar manner we hypothesized that adsorbate would be captured by inclusion and occlusion within the reformed floc after the ultrasonic energy had been withdrawn and defined this contaminant capture mechanism as a “sequestration” of the adsorbate. The process is more clearly described pictorially in Figure 1.

In order to test these hypotheses we performed a number of experiments to explore the ability of ultrasonic radiation to provide access to the IAC of a disrupted HFO floc and to “probe” the HFO system in order to provide insight into the mechanism

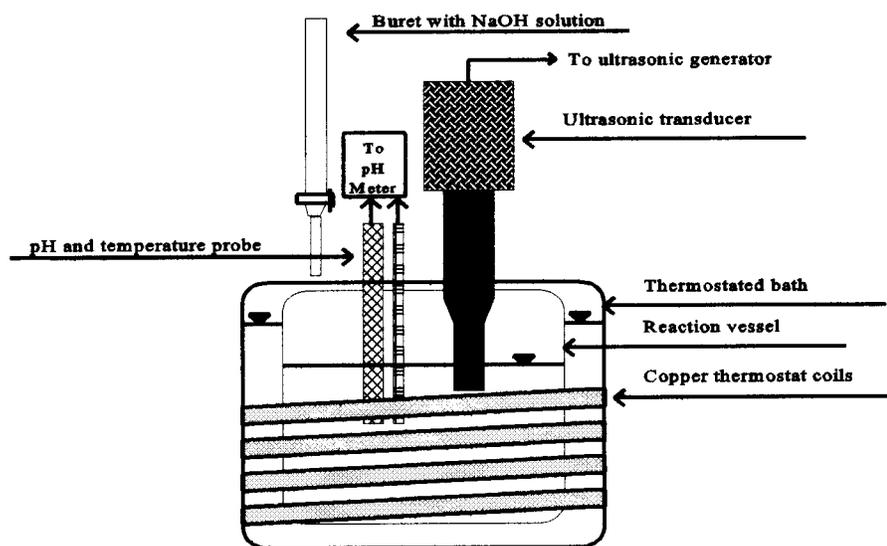


FIGURE 2. EXPERIMENTAL APPARATUS.

by which adsorption occurs and can be controlled.

EXPERIMENTAL

Materials

Equipment and chemicals (of the purity indicated) were supplied by Fisher Scientific, Inc. (Chicago, Illinois). Nitric and hydrochloric acids were of trace metal grade. Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ - CAS [10025-77-1]), sodium hydroxide (NaOH - CAS [1310-73-2]), and calcium carbonate (CaCO_3 - CAS [471-34-1]) were of certified ACS grade. Water of type I grade exhibiting resistivity of 18 megaohms or greater was polished by activated carbon adsorption and UV oxidation to remove residual organic contaminants. Nitrogen gas was provided by Superior Gas, Inc. (Cedar Falls, IA)

Equipment

A programmable Heat Systems, Inc., model XL-2020 ultrasonic generator and associated 1/2" probe type transducer hardware were utilized to produce the 20,000 Hz field. A

Fisher Accumet 15 pH meter calibrated with pH 4.00, 7.00, and 10.00 buffers was used to provide a continuous monitor of the hydronium ion concentration of the solutions. A Perkin Elmer model PE 3030 atomic absorption spectrophotometer was used to evaluate the iron and copper content of test solutions. Centrifugations were performed with an IEC model low speed centrifuge at approximately 3,000 revolutions per minute.

The apparatus used to investigate ultrasound induced adsorption-sequestration enhancement is presented in Figure 2.

Glassware utilized in all experimental procedures was cleaned by soaking overnight in 10% 1:1 HCl/HNO_3 to remove adsorbed metallic contaminants.

EXPERIMENTAL PROCEDURE

Fifty milliliters (ml) of a 1,000 ppm (1,000 mg/liter) solution of Fe^{3+} (as $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) in 0.1 molar NaNO_3 was pipetted from a stock solution maintained at 0°C (ice bath) to

prevent the premature hydrolysis of ferric ion. The 50 ml aliquot in a 400 ml beaker was warmed to 25°C in a constant temperature bath and then placed in a controlled temperature cooling cell to perform the trial. The magnetically-stirred solution containing 8.95×10^{-4} moles of iron was then rapidly neutralized with a carbonate-free sodium hydroxide solution (0.1 N or 0.01 N) prepared by gently bubbling N₂ gas through the water prior to and during solution preparation and use. A 0.1 N solution of HCl was also utilized as required to maintain the pH within 0.01 units of the desired level. After 20 minutes of maintenance at the desired pH (the pH of the solution normally drifts downward—apparently due to the release of protons into solution by the unstable amorphous HFO) a solution (one ml total volume) of cupric ion (Cu²⁺ as Cu(NO₃)₂) of the proper concentration was added to produce the desired molar fraction of copper to iron (10% or 30%). The resulting solution was again modified through addition of sodium hydroxide solution to obtain the desired pH. In ultrasonic trials, ultrasound was then applied for a total time period of three seconds at approximately 13 watts/cm² (260 watts/dm³—ultrasonic intensity determined by calorimetry—Mason, 1991) [20]. The pH of the solution remained steady during treatment and then generally decreased monotonically for the remainder of the experimental trial. The pH was maintained at the desired level for an additional 30 minutes after addition of the copper. The total pH maintenance time interval was one hour (an arbitrary optimal treatment interval for industrial waste treatment). At the end of the pH maintenance interval the flocculated solution was placed into a low speed centrifuge and centrifuged for thirty minutes. The supernatant fractions were decanted from the floc, combined in a 100 ml volumetric flask, and acidified by the

addition of five drops of concentrated nitric acid. One ml of calcium carbonate solution (6.3×10^{-5} moles) was added to the supernatant fractions, and the flask was brought to the final 100 ml volume. The floc fractions remaining in the centrifuge tubes were dissolved with a minimum quantity of 0.1 N HCl (2.0 ml) to which three drops of concentrated nitric acid had been added. The centrifuge tube washings were combined in a 100 ml volumetric flask with liquid fractions obtained from washing the reaction beaker, pH electrodes, and ultrasonic probe tip each with eight drops of 0.1 N HCl. The floc washings were combined with five drops of nitric acid and one ml of calcium carbonate solution (one ml— 6.3×10^{-5} Moles) in a 100 ml volumetric flask and the flask was brought to volume. Dilutions were performed as required on the floc and supernatant samples to obtain concentrations within the linear range of the PE-3030 atomic absorption spectrophotometer. Diluted samples were acidified with five drops of nitric acid, and one ml of calcium carbonate (0.063M in 1:5 HCl:H₂O) solution was added to each to suppress ionization of the iron during the atomic absorption analysis. Samples were placed into acid-washed and water-rinsed polypropylene plastic bottles fitted with screw top closures and stored frozen prior to atomic absorption analysis.

RESULTS AND DISCUSSION

The interaction of the ultrasonic field with heterogeneous particulate material held in suspension by constant stirring is anticipated to be complex. Exposure of the HFO floc to ultrasonic radiation resulted in immediate disruption of the particles to microscopically small sizes. The floc reforms rapidly (3-5 seconds) upon termination of irradiation and appears to be of essentially the same character as the pretreatment material;

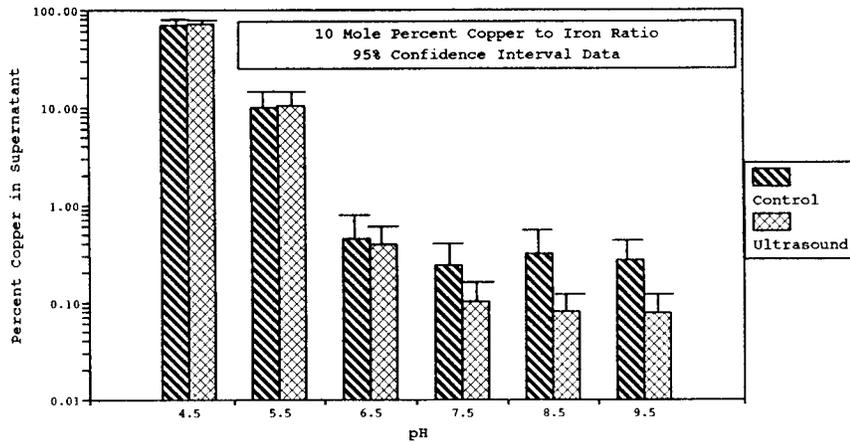


FIGURE 3. PERCENT COPPER (MASS COPPER IN SUPERNATANT/TOTAL MASS OF COPPER RECOVERED X 100) VS SOLUTION pH WITH 10 MOLE PERCENT COPPER TO IRON.

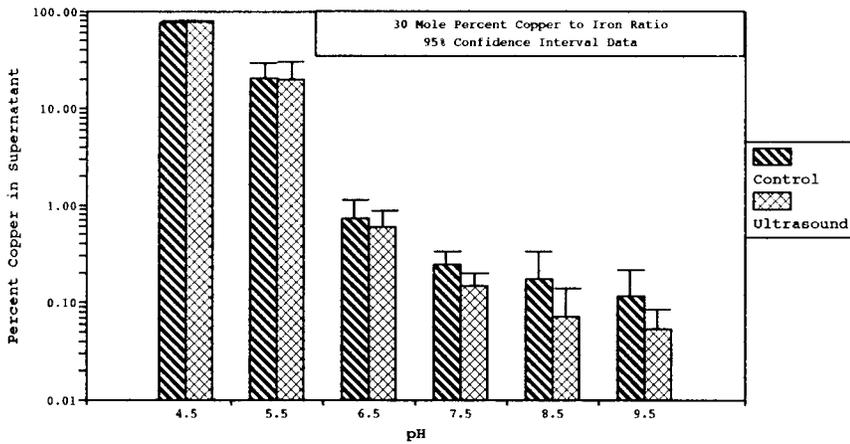


FIGURE 4. PERCENT COPPER (MASS COPPER IN SUPERNATANT/TOTAL MASS OF COPPER RECOVERED X 100) VS SOLUTION pH WITH 30 MOLE PERCENT COPPER TO IRON.

however, it is clear that fundamental changes in the nature of the floc have been instituted by the treatment. From the plots of experimental outcomes in Figures 3 and 4 and the data in Table 1 one can see the effect on the concentration of copper when solutions with copper to iron molar ratios of 10 and 30% are treated at pH 4.5-9.5.

In Figures 3 and 4 we have presented 95% confidence interval type plots but a more detailed statistical evaluation of the data to determine the distribution of the data revealed two features that make this type of

analysis inadequate. Evaluation of the skewness, kurtosis, and variability of the data revealed that the distribution of the plotted results was frequently skewed towards higher concentrations in the case of the control plots and that the variances between the control and ultrasound data sets were frequently non-uniformly distributed [21]. These factors led us to use a non-parametric statistical test to compare the ultrasound and control data sets: the Mann-Whitney U test for median homogeneity [22]. The results of the statistical evaluation are given in Table 1.

The data presented in Figures 3 and 4 and Table 1 demonstrate that ultrasonic treatment of HFO floc increases the ability of the treated material to remove copper ions from solution. The removal enhancement is strongly dependent upon pH. We have explained these findings in terms of an adsorption model in which the floc is comprised of a porous and/or permeable matrix whose adsorption sites are kinetically separated from the equilibrium adsorption state by restrictive film and pore diffusion. Disruption of the floc with the

ultrasonic radiation apparently results in exposure of the “internal adsorption capacity” of the floc to adsorbates in solution while simultaneously enhancing mass transfer via acoustic microstreaming and localized velocity fields associated with implosive collapse of cavitation bubbles. These exposed intrafloc adsorption sites are believed to be electron-deficient, presumably due to the inclusion within the floc at the time of formation of incompletely hydrolyzed ferric ion (i.e., $\text{Fe}(\text{OH})^{2+}$ and $\text{Fe}(\text{OH})_2^+$). Exposure of these electron-

TABLE 1. MANN-WHITNEY U TEST COMPARISON ANALYSIS OF THE PERCENT COPPER IN SOLUTION WITH AND WITHOUT ULTRASONIC TREATMENT.

pH	Cu/Fe Molar Ratio	Treatment Ultrasound (us) Control (cl)	Sample Size	p
4.5	10	us	6	0.5887
		cl	6	
	30	us	6	<0.0001
		cl	6	
5.5	10	us	6	0.0133
		cl	6	
	30	us	6	0.0840
		cl	6	
6.5	10	us	6	0.3095
		cl	6	
	30	us	9	0.9799
		cl	9	
7.5	10	us	8	0.0002
		cl	8	
		us	12	<0.0001
		cl	12	
8.5	10	us	16	<0.0001
		cl	15	
	30	us	9	0.0020
		cl	9	
9.5	10	us	16	<0.0001
		cl	15	
	30	us	12	0.0020
		cl	12	

Notes:

- US = Ultrasound, Cl = Control (no ultrasonic irradiation)
- A $p \leq 0.05$ is considered to be significant at the 95% confidence level
- Data calculated using Sigma Stat® microcomputer software [22]

deficient sites during and rapidly following ultrasonic disruption to solvated hydroxyl anions and then cationic metallic species is believed to give rise to an effective increase in the floc's surface charge (-) leading to enhanced adsorptive removal of copper from solution. At the same time the surface available for adsorption is increased due to particle size reduction during treatment.

CONCLUSIONS

Ultrasonic treatment of pre-formed adsorbents to enhance access to internal adsorption sites which are otherwise kinetically inaccessible appears feasible based on the outcome of this study. The level of enhancement attained is strongly dependent upon the solution pH at which treatment occurs, and careful control of solution pH is required to maximize removal efficiency. Ultrasonic treatment holds promise as a broadly-based methodology to modulate adsorption phenomenon in hazardous waste remediation and in industrial processing operations; however, the outcome of treatment is anticipated to be complex, requiring system-specific laboratory investigations.

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