Ministero dell'Ambiente e della Tutela del Territorio e del Mare – Direzione Generale Valutazioni Ambientali
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Oggetto: Invio modalità trattamento effluente sodiera
Allegati: AIA Sodiera Impianto trattamento sodiera - finale.pdf; Heavy metal removal by coagulation with seawater liquid bittern.pdf; Schema a blocchi impianto trattamento effluenti SO finale.pdf

Destinatari:
Gruppo Istruttore procedimento istruttorio ID127/434 (M. Mazzoni)

Facendo seguito alla richiesta pervenuta nel corso della riunione svoltasi in data 3 luglio u.s., invio l'aggiornamento tecnico in merito alle modalità di trattamento dell'effluente sodiera.

Cordiali saluti.

Il referente Controlli AIA
Francesco Posar

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RICEVUTO IL
31 LUG. 2013

Progetto d'impianto di trattamento degli effluenti - Sodiera

Premesse

L'impianto pilota per il trattamento degli effluenti sodiera ha fornito, in una serie di campagne di ricerca realizzate nel periodo marzo 2012 – marzo 2013, dei risultati operativi dai quali scaturiscono le seguenti indicazioni principali:

- possibile riduzione fino a 80÷90% del tenore in ammoniaca nell'effluente più ricco in tale composto (liquido in uscita dal settore distillazione); tale trattamento è stato effettuato con l'aggiunta di un ossidante quale l'ipoclorito di sodio;
- riduzione del piombo "libero" in fase liquida nell'effluente "liquido distillazione", tramite la sua inertizzazione mediante la riduzione della temperatura e del pH dell'effluente stesso a mezzo acqua di mare, piuttosto che a mezzo idrosolfuro di sodio; questo risultato conferma la funzione d'inertizzazione di metalli pesanti svolta dall'acqua di mare, come peraltro già indicato in letteratura (cfr. in proposito lo studio "*Heavy metal removal by coagulation with seawater liquid bittern*" che per comodità si allega alla presente relazione).

La sperimentazione effettuata ha inoltre confermato, come a suo tempo riportato nel documento inviato nel marzo 2008 alla Provincia di Livorno e successivamente al Gruppo Istruttore nel febbraio 2013, che l'acqua di mare recuperata dal processo ha la funzione e la capacità di regolare il pH degli effluenti liquidi della distillazione aventi elevata alcalinità; ciò in linea con la migliore tecnologia prevista nei documenti di riferimento europei ed in particolare le BREF specifiche per gli impianti produttivi vicino al mare (*Reference Document on Best Available Techniques for the Manifacture of Large Volume Inorganic Chemicals – Solids and Others Industry – Soda Ash, par. 2.3.10.3.2*).

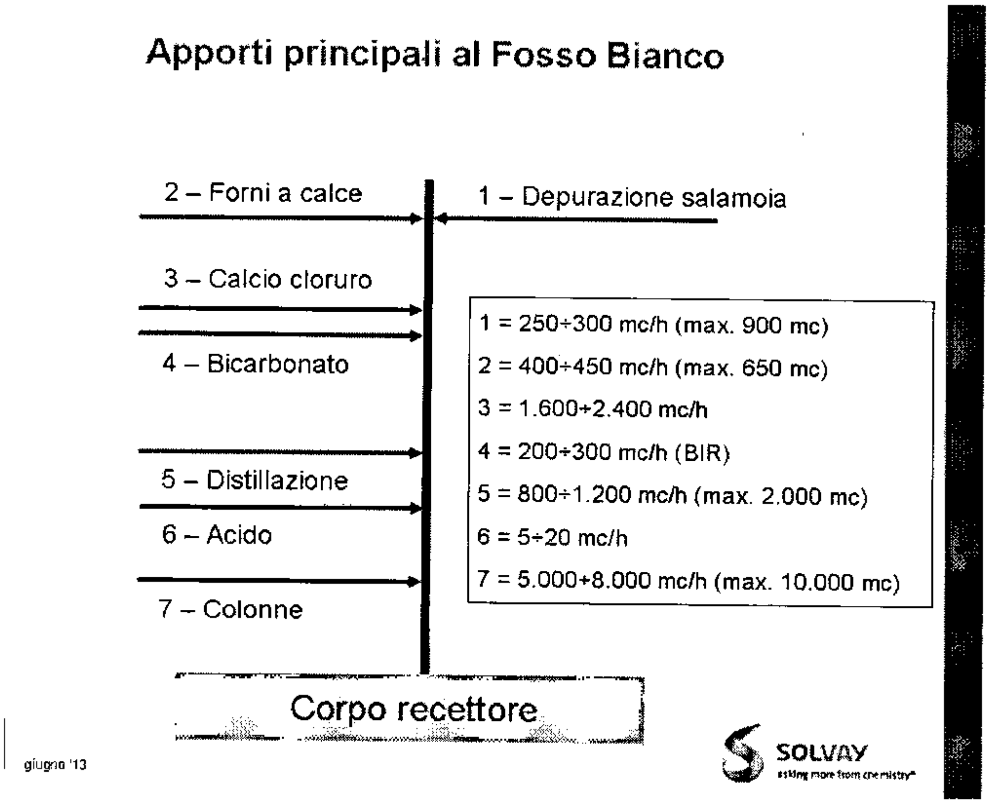
1. Schema degli effluenti di sodiera

Come presentato nel corso dell'incontro con il Gruppo Istruttore il 10 giugno 2013, gli effluenti sodiera sono costituiti dal coacervo dei seguenti flussi di acque di processo:

- dall'effluente depurazione salamoia
- dall'effluente forni a calce
- dall'effluente cloruro di calcio
- dall'effluente bicarbonato
- dall'effluente liquido distillazione
- dall'effluente colonne di bicarbonatazione

e dall'aggiunta di acido cloridrico per regolazione finale del pH.

Tali fussi si riuniscono nel canale industriale di scarico denominato Fosso Bianco, secondo lo schema di seguito riportato, prima di essere scaricati nel corpo ricettore "mare territoriale":



Apporti principali al Fosso Bianco

1 = 250÷300 mc/h (max. 900 mc)
2 = 400÷450 mc/h (max. 650 mc)
3 = 1.600+2.400 mc/h
4 = 200+300 mc/h (BIR)
5 = 800÷1.200 mc/h (max. 2.000 mc)
6 = 5÷20 mc/h
7 = 5.000+8.000 mc/h (max. 10.000 mc)

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In particolare:

- i flussi 1, 2, 3 e 4 dello schema precedente si congiungono assieme a monte del punto d'ingresso del liquido "distillazione" (DS);
- il liquido DS si immette nel coacervo dei suddetti 4 flussi; in caso d'emergenza per disservizio nel settore distillazione, il sistema prevede il suo invio verso la vasca di ripresa dove sono allocate delle pompe verticali per l'invio al bacino di diversione;
- alla fine, prima dell'immissione dell'acqua delle colonne di bicarbonatazione nel Fosso Bianco, è aggiunta la quantità d'acido cloridrico necessaria per la regolazione finale del pH.

2. Descrizione della proposta di progetto "impianto di trattamento effluenti"

L'impianto di trattamento in progetto prevede il trattamento di tutto il liquido DS con il recupero dell'ammoniaca e l'inertizzazione dei metalli pesanti presenti in forma solubile.

Come riportato nel documento inviato nel marzo 2008 alla Provincia di Livorno ed inviato anche al Gruppo Istruttore nel febbraio 2013, questo impianto di trattamento presenta molteplici profili ambientali positivi, a conferma della continua ricerca da parte della scrivente società di un miglioramento progressivo della sostenibilità delle proprie attività: infatti, l'utilizzo dell'acqua di mare in una delle fasi del nuovo trattamento, e precisamente come agente di condensazione nel condensatore di concentrazione a contatto diretto con la salamoia depurata, permetterà, da una parte, di aumentare il rendimento complessivo del processo di produzione di carbonato di sodio e, dall'altra, una riduzione dei consumi specifici di materie prime, quali acqua dolce, sale e energia, come specificato nella tabella allegata.

Tabella riduzione consumi materie prime							
Riduzione consumo NaCl (100% wt)		*Riduzione consumo CaO (100% wt)*		*Riduzione consumo vapore*		*Riduzione prellevo H2O dolce per salamola*	
t/h	*t/anno*	*t/h*	*t/anno*	*t/h*	*t/anno*	*m3/h*	*m3/anno*
8,8	77.088	0,2	1.752	7,8	68.328	26,4	231.264

2.1. Descrizione impianto di trattamento effluenti

L'impianto di trattamento reflui proposto permette:

- nella sezione di concentrazione salamoia
    - la riduzione del tenore di ammoniaca nel liquido DS;
    - la produzione di uno "slurry" di cloruro di sodio da riutilizzare per aumentare l'efficienza del processo sodiera[1];
- nella sezione di reazione
    - l'inertizzazione dei metalli pesanti solubili;
    - una prima grossolana riduzione dell'alcalinità residua;
    - l'eventuale eliminazione di ammoniaca (sistema di guardia);
    - l'eventuale eliminazione degli agenti ossidanti quando il sistema di guardia è attivo.

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[1] La salamoia proveniente da Ponteginori allo stabilimento di Rosignano Solvay è quasi satura in cloruro di sodio. Una volta entrata nel ciclo produttivo della Sodiera, i sistemi di trattamento effettuati per eliminare il calcio e il magnesio e ridurre la concentrazione in solfato ne provocano una prima diluizione (indicativamente da 310 kg NaCl/m^3 a 300 kg NaCl/m^3). In seguito, negli scrubber, lavatori, a causa della condensazione del vapor d'acqua, la salamoia si diluisce ulteriormente fino a raggiungere un fattore di diluizione pari al 5% all'ingresso degli assorbitori (circa 295 kg NaCl/m^3).
La diluizione della salamoia ammoniacale provoca una riduzione della forza motrice per la precipitazione del bicarbonato e quindi tale diluizione diminuisce il rendimento complessivo dell'impianto. L'aggiunta di uno slurry di sale consente il ripristino della corretta forza motrice.

Con riferimento allo schema a blocchi riportato in fondo al presente documento (e comunque allegato in file separato), nella sezione di concentrazione salamoia, il liquido di distillazione (liquido DS, fluido 1) è alimentato verso due nuovi degasatori posti in parallelo e operanti sotto vuoto. Tali apparecchiature permettono di ridurre la temperatura degli effluenti liquidi di circa 10°C, con conseguente produzione di vapor acqueo e ammoniaca (fluido 3) e liquido DS degasato (fluido 2). Quest'ultimo è inviato per successivo trattamento nella sezione di reazione. Il fluido 3 è inviato in uno scambiatore di calore a fascio tubiero (lato mantello) per il riscaldamento della salamoia di processo (lato tubi - fluido 4). Il vapore ammoniacale condensato (fluido 10) è opportunamente recuperato nell'impianto sodiera. La salamoia uscita scambiatore (lato tubi - fluido 5) è inviata al cristallizzatore. In tale apparecchio avviene l'evaporazione della soluzione salina, con conseguente produzione di slurry (fluido 6) e produzione di vapore (fluido 7) che, con i suoi trascinamenti di salamoia di processo, è condensato per contatto diretto con acqua di mare proveniente dalle colonne del settore bicarbonatazione (fluido 8). L'uscita del condensatore (fluido 9) è avviata alla sezione di reazione.

Nella sezione di reazione, il liquido DS degasato (fluido 2) e il condensato (fluido 9) sono alimentati nel primo tratto del fosso bianco, che funge da reattore a pistone fornendo sufficiente tempo di contatto per l'inertizzazione dei metalli pesanti. La sezione di reazione è completata da un sistema di guardia tramite il dosaggio d'ipoclorito di sodio per ridurre la concentrazione di ammoniaca in caso di malfunzionamento del sistema di vuoto e conseguente dosaggio di un agente riducente (esempio: acqua ossigenata, idrosolfuro di sodio, ...) per l'eventuale eliminazione del cloro attivo residuo.

Si allega una tabella riassuntiva di un tipico bilancio di materia dello schema a blocchi.

Tabella schema a blocchi impianto trattamento effluenti liquidi Sodiera

Flusso		*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*
		Liquido uscita distillazione	*Liquido uscita Degasatori*	*Vapore*	*Salamoia di processo*	*Navetta salamoia*	*Slurry NaCl*	*Vapori di processo*	*Acqua di mare ingresso*	*Condensato*	*Condense*
Portata	*m3/h*	1.102	1.076	105.600	36,3	6.000	16,9	259.000	5.040	5.059	19
Densità liquido	*kg/m3*	1.078	1.086		1.200		1.200		1,030	1.030	1,000
Temperatura	*°C*	80	69,3	69,3	30	60	58,6	52,4	23	25	67,6

L'impianto di trattamento funzionerà a ciclo continuo per 24 ore al giorno, permettendo anche la realizzazione delle economie prima citate.

2.2. Stima dei costi d'investimento e dei tempi di realizzazione

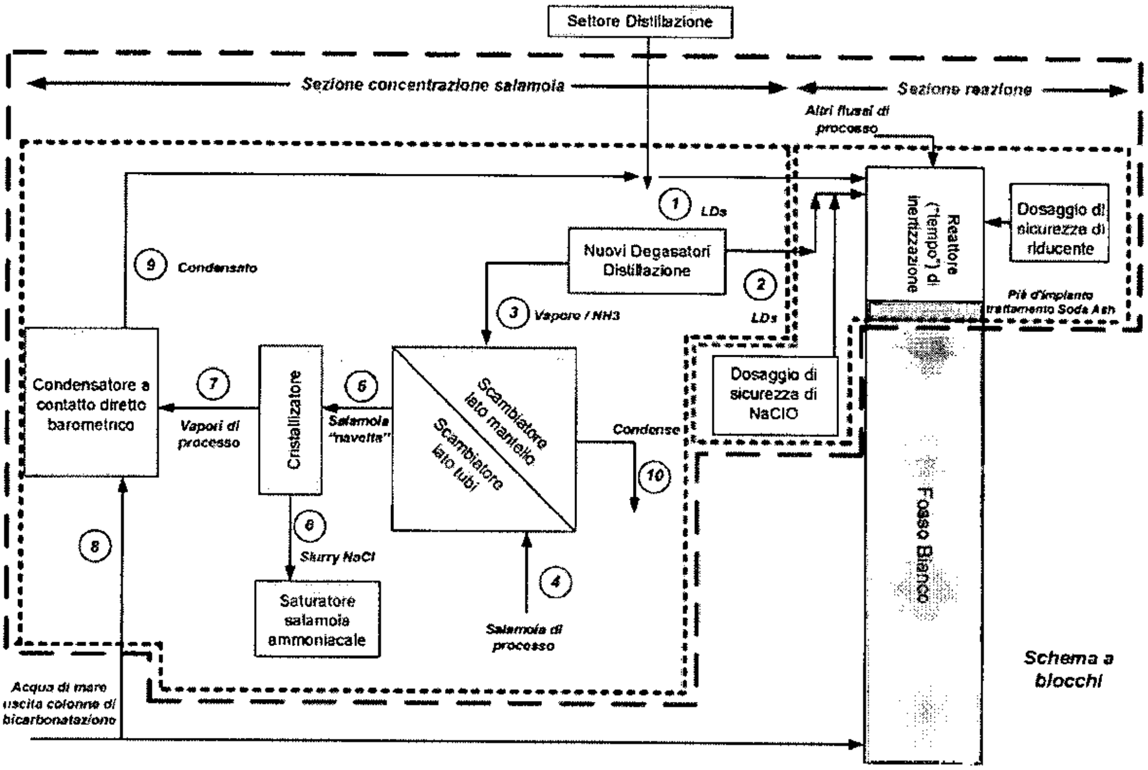
Una stima preliminare dell'investimento totale per la realizzazione dell'impianto di trattamento si aggira intorno ai 10 M€, come di seguito specificato:

Item	*Note*	*Montante*	
Ingegneria	*Ing. di base e di dettaglio, supervisione montaggi, studi analisi rischi, permessi...*	1.410.000	€
Apparecchi statici e relativo montaggio	*Riserve, scambiatori, Evaporatori...*	2.050.000	€
Apparecchi meccanici e relativo montaggio	*Pompe*	500.000	€
Lavori civili/strutture		1.550.000	€
Tubazioni e valvole manuali		1.600.000	€
Lavori elettrici		600.000	€
Lavori strumentali e automazione	*Misure, valvole automatiche, analizzatori...*	850.000	€
Lavori diversi	*Coibentazioni, verniciature*	200.000	€
Imprevisti	*10%*	880.000	€
TOTALE		9.640.000	€

I tempi di realizzazione dell'impianto di trattamento e suo avviamento sono stimati in almeno 24 mesi, da considerarsi a partire dall'accettazione formale del progetto e relativa autorizzazione.

2.3. Schema a blocchi impianto di trattamento

IMPIANTO TRATTAMENTO EFFLUENTI LIQUIDI SODIERA



HEAVY METAL REMOVAL BY COAGULATION WITH SEAWATER LIQUID BITTERN

By G. M. Ayoub,[1] Member, ASCE, L. Semerjian,[2] A. Acra,[3] M. El Fadel,[4] and B. Koopman[5]

ABSTRACT: Soluble heavy metals present in water could be deleterious to health, and as a result, their discharge into surface waters has been regulated internationally. Many processes for the removal of heavy metals from water and wastewater have been investigated. Coagulation and precipitation are the processes that have been reported to be most effective in the removal of heavy metals. In this study, seawater liquid bittern (LB), as an inexpensive source of magnesium, added to wastewater alkalized with lime or caustic soda is investigated as a possible coagulant. The experiments covered tests on eight metals: arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. The lime-LB process culminated in high removals (>90%) for cadmium, chromium, lead, mercury, and zinc and reasonably good removals (71, 82, and 75%) for arsenic, copper, and nickel, respectively. These results were superior to those obtained using the caustic-soda-LB process. The concurrent presence of different metals in solution has been shown to have a minor effect on removal efficiencies for most metals. However, in the case of nickel, removal was appreciably increased by 18.5%. Also, higher concentrations of a single metal showed higher removal efficiencies.

INTRODUCTION

Heavy metals may reach watercourses either through a variety of geochemical processes or by the direct discharge of municipal and industrial wastewater. Anthropogenic activities such as manufacturing, construction, agriculture, and transportation can be regarded as the main sources of metal-rich wastewaters. At elevated concentrations, soluble metal compounds can be deleterious to human health as well as to aquatic and marine ecology [Lester 1987; Water Environment Federation (WEF) 1994]. Because of the associated adverse effects, international regulatory agencies have promulgated effluent standards limiting heavy metal discharges into surface waters as well as into municipal sewers. However, the cost of compliance with pollution control legislation is extremely high in most cases and sometimes unaffordable, particularly by small industries (WEF 1994).

Considering the severe impact of wastewater pollution, it is essential to develop simple and economic strategies for wastewater treatment that are applicable to and affordable by developing countries. Specifically, there is a great need to develop appropriate means of heavy metal removal. In previous studies, seawater bittern was found to be an effective and economic source of magnesium ions (Ayoub et al. 1999, 2000) that may be used in the treatment of municipal and industrial wastewaters. Substantial removal of suspended solids, chemical oxygen demand (COD), nutrients, and color have been attained using liquid seawater bittern (Wang and Chen 1983; Shin and Lee 1997; Ayoub et al. 1999, 2000). Metal removal has not been assessed using liquid bittern (LB); however, it is expected that substantial removal should be attained because heavy metals are associated with settling particles to a great extent (Chen and Hendricks 1974; Idelovitch 1978; Ødegaard 1989, 1992, 1995; Morgan and Stumm 1991; Van Nieuwenhuiyzen et al. 1999).

The objective of the proposed study is to evaluate the effectiveness of seawater LB to remove heavy metals, as a step toward chemical purification of wastewater, by the application of a simple and inexpensive technology (Semerjian 2000). In principle, the method is based on the use of magnesium salts contained in the bittern to serve as a coagulating agent under alkaline conditions (pH 11.0–11.5).

The significance of the proposed research lies in its potential for removing toxic heavy metals from wastewater in a simple, inexpensive, and easily controlled manner. In developing countries, LB is produced by the salt-making industry; however, it is not utilized for any purpose and is discarded. This liquor may be saved and advantageously used for the proposed treatment. Heavy metal removal, employing the proposed method, will be a complimentary asset to the simultaneous chemical treatment of wastewaters in terms of organic pollutants, suspended solids, nutrients, and color (Wang and Chen 1983; Shin and Lee 1997; Ayoub et al. 1999, 2000). Moreover, effective bacterial destruction will also be achieved as a result of the high pH level maintained throughout the operation of the process (Riehl et al. 1952; Grabow et al. 1978; Idelovitch 1978; Vrâle 1978; Ødegaard 1987, 1989, 1995; Ayoub et al. 1999, 2000).

MATERIALS AND METHODS

Production of LB

The seawater concentrate LB was obtained by the solar evaporation of seawater from an initial volume and density of 125 L and 1.027 kg/L, respectively, to a final volume and density of approximately 1.3 L and 1.2705 kg/L. The seawater was collected from the Mediterranean Sea from the beach facing the American University of Beirut (AUB) campus. The evaporation process was carried out using an array of metallic pans installed adjacent to the Environmental Engineering Research Center (EERC) and in accordance with the criteria and critical density indices reported by Abdallah (1996). In the course of the solar evaporation process, complete deposition of calcium salts ($CaCO_3$ and $CaSO_4$) took place in the first pan. Crystallization and settling out of most of the NaCl present in the seawater occurred in the second plan, thus ending the evaporation process. The produced magnesium-rich LB was collected and stored in a 1.5-L polyethylene container at

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Note. Associate Editor: Makram Suidan. Discussion open until August 1, 2001. To extend the closing date one month, a written request must be filed with the ASCE Manager of Journals. The manuscript for this paper was submitted for review and possible publication on April 14, 2000; revised September 12, 2000. This paper is part of the *Journal of Environmental Engineering*, Vol. 127, No. 3, March, 2001. ©ASCE, ISSN 0733-9372/01/0003-0196–0207/$8.00 + $.50 per page. Paper No. 22293.

TABLE 1. Physicochemical Characteristics of LB

Parameter (1)	Measured value ± standard deviation[a] (2)
pH	6.78 ± 0.1
Density	1.2705 ± 0.1
TDS	396,000 ± 1,556
EC	794,000 ± 2,828
Mg^{2+}	53,473 ± 373
Ca^{2+}	0 ± 0
Cl^-	279,913 ± 203
Na^+	70,883 ± 790
K^+	14,000 ± 707
SO_4^{2-}	46,278 ± 1,218

[a] All values are expressed in milligrams per liter except for pH (pH units), density (grams per milliliter at 20°C), and electrical conductivity (μmhos/cm at 25°C). Conversion factors for concentration units in milligrams per liter to milliequivalent per liter are Mg^{2+} = 0.0823, Na^+ = 0.0435; Cl^- = 0.0282; and SO_4^{2-} = 0.0208.

room temperature to be used later as the source for the magnesium coagulant. The physicochemical characteristics of the LB are summarized in Table 1.

Choice of Matrix

To capture the sole effect of Mg^{2+} ions within the LB on metal removal, a magnesium-free matrix was used at the preliminary stage of the experimental plan. Previous literature (Ayoub et al. 1992, 1999) as well as actual sampling and analysis of municipal wastewater (MWW) samples revealed that sewage contains a significant amount of magnesium salts that might have originated from either seawater intrusion or dolomitic rock formations.

Trial experiments were carried out using suspensions of clay and finely ground bread crumbs in order to find a simple magnesium-free matrix. After determining the matrix-specific optimum Mg^{2+} dose, several trial experiments on the clay suspensions revealed the difficulty of completely acid digesting the clay, a key step in metal analysis, because of its inorganic chemical nature. Moreover, trials revealed that the clay particles, by themselves, were serving as a coagulant aid. Therefore, to avoid interference and bias, this matrix was discarded.

The second choice of matrix was a suspension of finely ground bread crumbs. Distilled water was used as the diluent to avoid the initial containment of magnesium salts in the matrix and to minimize the presence of carbonates, thus reducing $CaCO_3$ formation upon addition of lime. By doing so, the formation of mainly $Mg(OH)_2$ flocs, originating from the added bittern volumes, was ensured. After testing for its magnesium content, acid digestibility, and adsorption properties, the matrix was adopted for experimentation at the preliminary stage of the testing plan.

A more intensive analytical plan was executed following the Mg^{2+}-free matrix experiments using MWW as an actual environmental matrix. Throughout the course of the study, fresh samples of MWW were collected in the morning from an open sewer outfall at Ras Beirut in the vicinity of the AUB and carried to the EERC for use in the experimental work. The physicochemical characteristics of the collected MWW samples for use during the course of the experiments are given in Table 2.

Choice of Metals

Within the experimentation program, eight metals were subjected to testing: arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc. The choice of metals was based on the following factors:

- Prevalence in common municipal and industrial effluents
- Toxicity and pollution induction characteristics
- Classification as "priority pollutants" by the U.S. Environmental Protection Agency (USEPA)

The following chemicals, supplied by J. T. Baker as 1,000-μg/mL stock standard metal solutions, were used as the source of the various metals: As_2O_3, $Cd(NO_3)_2$, $Cr(NO_3)_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Hg(NO_3)_2$, $Ni(NO_3)_2$, and ZnO. In all cases the solvent was 0.5 mol/L nitric acid.

Experimental Procedures

Eleven sets of laboratory experiments were conducted on freshly alkalized MWW samples. The objective of each set was to evaluate and compare metal removal patterns employing hydroxide precipitation or LB coagulation/hydroxide precipitation. Hydroxide precipitation was induced by adding either 4% (w/v) caustic soda (NaOH) or 6.6% (w/v) slaked lime [$Ca(OH)_2$] to assess the effect of the alkalization mode employed. The experiments conducted on MWW were referred to as jar tests I-A and I-B through XI-A–XI-C.

Before proceeding with the evaluation of metal removal trends, jar tests I-A and I-B were performed to determine the matrix-specific optimum dose of Mg^{2+} ions needed to efficiently settle the suspended solids and flocs in the presence of an alkalizing agent. Turbidity or total suspended solids (TSS) removal patterns were selected to reflect potential metal removal patterns because settling particles play a dominant role in binding heavy metals and transferring them into deeper layers. Thus, achieving a high level of TSS removal should result

TABLE 2. Physicochemical Characterization of Collected MWW

Jar test (1)	pH (2)	TDS (3)	EC (4)	Turbidity (5)	Cl (6)	Ca^{2+} (7)	Mg^{2+} (8)	Alkalinity		
								OH (9)	CO_3^- (10)	HCO_3^- (11)
II	7.75	884	1,770	210	195	85.3	34.0	0	0	412
III	7.71	941	1,879	220	200	88.2	34.0	0	0	413
IV	7.77	732	1,462	380	197	70.0	34.0	0	0	424
V	7.83	743	1,486	180	185	68.2	34.0	0	0	432
VI	7.93	764	1,534	195	188	100.0	16.8	0	0	430
VII	7.66	713	1,425	250	192	84.0	29.2	0	0	408
VIII	7.91	728	1,534	240	113	104.0	9.7	0	0	400
IX	7.83	616	1,235	146	149	104.0	21.9	0	0	370
X	8.09	953	1,902	158	330	72.2	41.3	0	0	412
XI	8.08	1,170	2,340	150	299	74.2	54.7	0	0	410
XII	7.86	752	1,505	210	256	80.2	26.7	0	0	516

Note: All values are expressed in milligrams per liter except for pH (pH units), electrical conductivity (μmhos/cm at 25°C), turbidity (NTU), and alkalinity (milligrams per liter as $CaCO_3$).

in significant reductions of heavy metals as well as other contaminants such as oil and grease, phosphorus, COD, biochemical oxygen demand (BOD), and pathogens (Booker et al. 1996). The extent of metal binding is influenced in part by the affinity of the metal for the particle surface and also by the speciation of the metal in solution (Chen and Hendricks 1974; Idelovitch 1978; Ødegaard 1989, 1992, 1995; Morgan and Stumm 1991; Van Nieuwenhuiyzen et al. 1999).

Jar tests II–IX consisted of triplicate trial experiments to assess and compare individually added metal removal patterns by hydroxide precipitation or LB coagulation/hydroxide precipitation. Jar tests II–IX respectively assess the removal patterns of nickel, chromium, copper, lead, zinc, cadmium, arsenic, and mercury. Triplicate tests (A–C) were conducted for each test set.

In jar tests X-A–X-C nickel, chromium, copper, lead, zinc, and cadmium were concurrently added to the MWW and the removal of each metal assessed. Again, the objective of this experiment was to establish potential enhancement or hindrance mechanisms exerted by the mixture of metals.

Finally, the metal removal efficiencies with respect to increasing initial concentrations of metals were evaluated with jar tests XI-A–XI-C. In this set of experiments, gradually increasing doses of nickel were added to the alkalized MWW and the subsequent nickel removal patterns were evaluated and compared. Table 3 summarizes and justifies the experiments conducted on alkalized MWW.

Jar Tests

Two standard jar test apparatuses (model 300, Phipps and Bird, Inc.) were employed for the experimental coagulation-flocculation process. Each apparatus holds six stainless steel stirrers and paddles having heights of 25 mm and diameters of 76 mm. The jars are made of acrylic plastic and have dimensions of 115 × 115 × 250 mm.

The jar tests were conducted under controlled laboratory conditions by operating the stirrers first for a duration of 1 min at a mean velocity gradient value G of 135 s^{-1} (100 rpm) for flash mixing. The speed was then reduced to a G of 23 s^{-1} (30 rpm) to allow a 20-min contact time for coagulation-flocculation to take place. The stirrers were then stopped, and a 30-min quiescent settling period was initiated, at the end of which about 300 mL of processed suspensions or clarified supernatants were decanted to be used for further analysis of total metals, pH, turbidity, total dissolved solids (TDS), and electrical conductivity (EC). Sludge, if produced, was also digested and subjected to total metal analysis.

Replicate jar tests were conducted on the same day, using the same batch of prepared and alkalized matrix.

Experiments on MWW

For every jar test set, a fresh 20-L sample of MWW was collected and transported to the EERC to be used in the experimental work. At the EERC, the sewage was transferred to a glass container and subjected to constant mechanical stirring to ensure sample homogeneity. The homogeneous sample was handled in accordance with the test objectives. Aliquots of 1 L of MWW were transferred into each jar, the necessary chemicals added, and the standard jar tests initiated.

Jar Test I (A and B): Determining Optimum Mg^{2+} Dose

Aliquots of 1 L of MWW were transferred into each of the six jars. The contents of the jars in test I-A were initially alkalized to a pH of 11.4 ± 0.1 with NaOH, whereas those in test I-B were initially alkalized to the same pH using $Ca(OH)_2$. Caustic soda solution was added at an average dose of 18 mL/L while slaked lime was added at an average dose of 20 mL/L. Predetermined serial doses of LB were then added to respectively add Mg^{2+} concentrations of 0, 53.5, 107, 160.5, 214, and 267.5 mg/L to each jar of the two sets, and the tests were initiated.

TABLE 3. Summary of Experiments Conducted on Alkalized MWW

Jar test (1)	Objective (2)
I (A–C)	Determination of optimum dose of magnesium ions
II (A–C)	Assessment and comparison of nickel removal patterns using alkalization or alkalization-LB coagulation-precipitation
III (A–C)	Assessment and comparison of chromium removal patterns using alkalization or alkalization-LB coagulation-precipitation
IV (A–C)	Assessment and comparison of copper removal patterns using alkalization or alkalization-LB coagulation-precipitation
V (A–C)	Assessment and comparison of lead removal patterns using alkalization or alkalization-LB coagulation-precipitation
VI (A–C)	Assessment and comparison of zinc removal patterns using alkalization or alkalization-LB coagulation-precipitation
VII (A–C)	Assessment and comparison of cadmium removal patterns using alkalization or alkalization-LB coagulation-precipitation
VIII (A–C)	Assessment and comparison of arsenic removal patterns using alkalization or alkalization-LB coagulation-precipitation
IX (A–C)	Assessment and comparison of mercury removal patterns using alkalization or alkalization-LB coagulation-precipitation
X (A–C)	Assessment and comparison of nickel, chromium, copper, lead, zinc, and cadmium removal patterns using alkalization or alkalization-LB coagulation-precipitation
XI (A–C)	Assessment and comparison of removals of varying doses of nickel using alkalization or alkalization-LB coagulation-precipitation

Jar Tests II–IX: Assessing Removals of Individually Added Metals

From a fresh 6-L batch of MWW, to aliquots of 1 L each were transferred into two separate jars (designated as J1 and J2) and two aliquots of 2 L each were transferred into another two separate beakers. The content of each beaker was alkalized to a pH of 11.4 ± 0.1 using either NaOH or $Ca(OH)_2$. Two aliquots of 1 L from each beaker were taken into four separate jars (designated as J3, J4, J5, and J6) to obtain a total number of six jars. J1 was treated as a control for the overall experiment. Finally, the standard jar test procedure was initiated.

Jar Test X: Assessing Removals of Concurrently Added Metals

The sequence and amounts of metal solutions as well as LB applied and procedures were identical to the experiments dealing with individually added metals. However, the major difference was that in this experimental set, six metals were concurrently added to the matrix.

Jar Test XI: Assessing Removals of Varying Initial Concentrations of Nickel

In an attempt to evaluate metal removal efficiencies in relation to increasing initial concentrations of metals, gradually increasing doses of nickel were added to the experimental matrix. Thus, 4 L of MWW were alkalized with NaOH and another 4 L with $Ca(OH)_2$. One-liter aliquots of alkalized MWW were transferred into two sets of four separate jars, and volumes of 1, 2, 4, and 6 mL from the stock nickel solution (1,000 μg/mL) were dispensed into each jar. Details of this experiment are summarized in Table 4.

Analytical Procedures

An extensive physicochemical characterization of each experimental matrix as well as of the LB was conducted. Tested parameters were the pH, turbidity, density, TDS, EC, BOD, COD, alkalinity, nitrates, orthophosphates, sulfates, chlorides, magnesium hardness, calcium hardness, sodium, potassium, and total metals.

In addition, at the end of each jar test, aliquots of processed suspensions or clarified supernatants decanted from each jar were analyzed for the following parameters: pH, TDS, EC, turbidity, and the metal under assay. Moreover, sludges, when produced, were acid-digested and analyzed for their metal content.

All analytical tests were performed in accordance with the *Standard methods for the examination of water and wastewater* [American Public Health Association (APHA) et al. 1995]. A list of the analyzed parameters as well as types and references of the analytical methods is presented in Table 5.

TABLE 4. Jar Specifications in Experiment XI

Jar number (1)	Alkalizing agent (2)	Added volume of nickel (mL) (3)	Added concentration of nickel (μg/L) (4)	Added volume of LB (mL) (5)
1	NaOH	1	1,000	2
2	NaOH	2	2,000	2
3	NaOH	4	4,000	2
4	NaOH	6	6,000	2
5	$Ca(OH)_2$	1	1,000	2
6	$Ca(OH)_2$	2	2,000	2
7	$Ca(OH)_2$	4	4,000	2
8	$Ca(OH)_2$	6	6,000	2

TABLE 5. List of Analyzed Parameters and Adopted Analytical Procedures

Parameter (1)	Type of analysis (2)	APHA reference method (3)
pH	Potentiometry	4500-H^+ B
TDS	Potentiometry	2510 B
EC	Potentiometry	2510 B
BOD	Potentiometry	5210 B
COD	Closed reflux/colorimetry	5220 D
Density	Gravimetry	NA
Turbidity	Nephelometry	2130 B
Chlorides	Argentometric titration	4500-Cl^- B
Calcium hardness	EDTA titration	3500-Ca D
Magnesium hardness	EDTA titration	3500-Mg E
Alkalinity	Acid titration	2320 B
Sulfates	Colorimetry	4500-SO_4^{2-} E
Nitrates	Colorimetry	4500-NO_3^- E
Orthophosphates	Colorimetry	4500-P E
Sodium	Flame emission photometry	3500-Na D
Potassium	Flame emission photometry	3500-K D
As, Cd, Cr, Cu, Ni, Pb, Zn	Acid digestion/AAS	3030 E/3113 B
Hg	Acid digestion/ICP-MS	3030 E/3120 B

Note: NA = not applicable; EDTA = ethylene diamine tetra acetic acid; AAS = atomic absorption spectrophotometry; and ICP-MS = inductively coupled plasma-mass spectrophotometry.

RESULTS AND DISCUSSION

Determination of Optimum Magnesium Dose for Magnesium-Free Matrix

The results of the tests performed to determine the matrix-specific optimum Mg^{2+} dose using a magnesium-free matrix are shown in Fig. 1. The optimum dose was selected as that equivalent to the amount of Mg^{2+} ions needed to efficiently settle the suspended particles in the alkalized matrix. Turbidity or TSS removal patterns were selected to reflect potential metal removal patterns because most of the metals that can be removed by LB addition above alkalization are associated with the suspended particles within the matrix.

Fig. 1 reveals that the Mg^{2+} ion concentration at which the highest turbidity removal percentage was achieved is about 134 mg/L for the employed matrix, regardless of the alkalizing agent. At this Mg^{2+} ion concentration, turbidity removal was on the order of 91.7% ± 1.3 when the matrix was alkalized with NaOH and 97.2% ± 1.1 when the alkalizing agent was $Ca(OH)_2$. Percentages were computed on the basis of the original turbidity in the raw settled suspension measured to be 23 ± 3 nephelometric turbidity units (NTU).

Determination of Optimum Magnesium Dose for MWW

To determine the matrix-specific optimum Mg^{2+} dose, fresh samples of MWW were alkalized with either NaOH or $Ca(OH)_2$ and predetermined serial doses of LB equivalent to Mg^{2+} concentrations of 0, 53.5, 107, 160.5, 214, and 267.5 mg/L were respectively dispensed into the alkalized matrix. Fig. 2 reveals that the highest turbidity removals were achieved at an Mg^{2+} concentration of about 107 mg/L, regardless of the employed alkalization mode. For samples al-

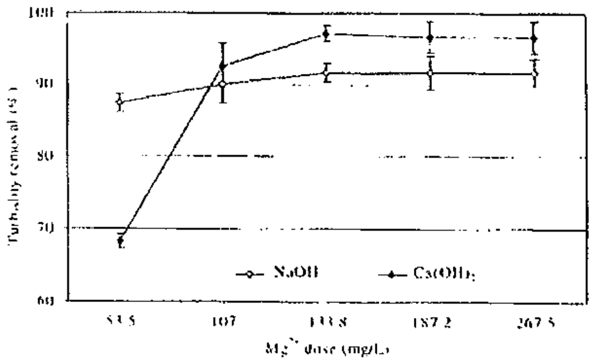

FIG. 1. Average Turbidity Removal Percentages as Function of Added Mg^{2+} Dose

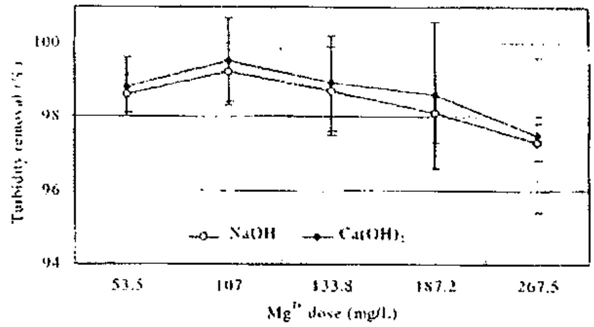

FIG. 2. Average Turbidity Removal from MWW as Function of Added Mg^{2+} Dose

kalized with caustic soda, attained turbidity removals were 95.25% ± 1.2, 98.6% ± 0.5, 99.2% ± 0.8, 98.7% ± 1.2, 98.1% ± 0.8, and 97.3% ± 0.5 for added Mg^{2+} concentrations of 0, 53.5, 107, 160.5, 214, and 267.5 mg/L, respectively. In the case of lime treatment, turbidity removals were 97.8% ± 1.1, 98.8% ± 0.8, 99.5% ± 1.2, 98.9% ± 1.3, 98.6% ± 2.0, and 97.5% ± 2.1, respectively.

The results are similar to the findings reported by Ayoub et al. (1999) on studies related to MWW that showed turbidity removal values of 99.1 and 99.2% for NaOH and $Ca(OH)_2$ alkalization, respectively, in the presence of the same optimum dose of LB.

Percentages are computed on the basis of the original turbidity in the settled raw MWW (Jar I). Clarification is, basically, attributed to the formation and precipitation of $CaCO_3$ and $Mg(OH)_2$ flocs at pHs of 9.5 and 11.2–11.5, respectively (Ayoub et al. 1999, 2000).

Evaluation of Physicochemical Characteristics of Clarified Effluents

pH

The addition of magnesium ions into the alkalized MWW samples resulted in a gradual decrease in the pH of the clarified elements. The hydroxyl ions reacting with the supplemented Mg^{2+} ions led to the formation and precipitation of $Mg(OH)_2$, thus reducing pH values. On the average, pH values decreased by 4.5% when LB was added to MWW samples alkalized with NaOH and 5.8% when the alkalizing agent was $Ca(OH)_2$. Ayoub and Koopman (1986) and Ayoub et al. (1999, 2000) reported similar observations upon the addition of seawater or LB to alkalized wastewaters.

Turbidity

Significant turbidity removals from MWW were achieved by the sole employment of alkalization. This phenomenon is attributed to the formation of $CaCO_{3(s)}$ flocs at a pH of 9.5, induced by the initial presence of alkalinity in the raw sewage. Also, the magnesium salts, naturally contained in the MWW samples, partially induced the formation of $Mg(OH)_2$ precipitates. Fig. 3 depicts the average turbidity removals achieved simply by alkalizing the samples. Percentages were computed on the basis of the original turbidity value in the raw settled wastewater (J1).

It can be concluded that alkalization with lime generally results in higher percentages of turbidity removal as compared to caustic soda alkalization. This trend is mainly due to the superior settling properties of the floc produced from the lime treatment process. The resulting sludge occupies less volume than that obtained from the caustic soda treatment and has higher suspended solid concentrations. This is one reason lime alkalization is generally favored over caustic soda alkalization.

Upon the addition of LB to the alkalized MWW samples, even higher turbidity removals were attained (Fig. 4). These higher efficiencies may be attributed to the two most prominent advantages associated with LB: (1) The enriched magnesium content (1.32–2.85 mol/kg at 29.1–34.9°Bé); and (2)

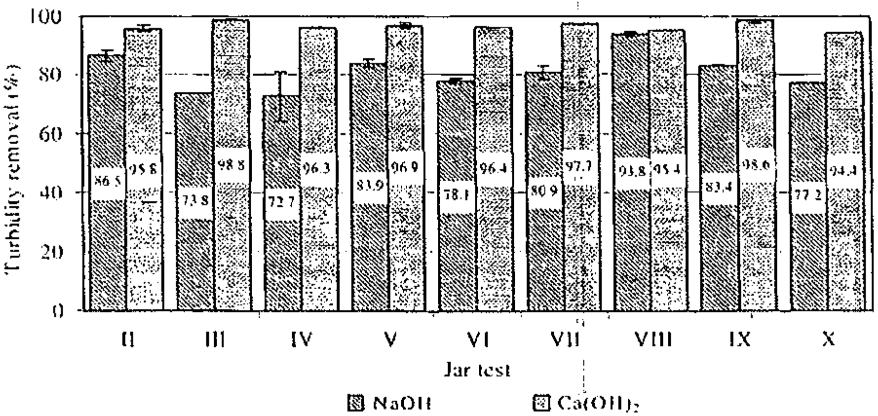

FIG. 3. Average Turbidity Removal Percentages by Sole Employment of Alkalization

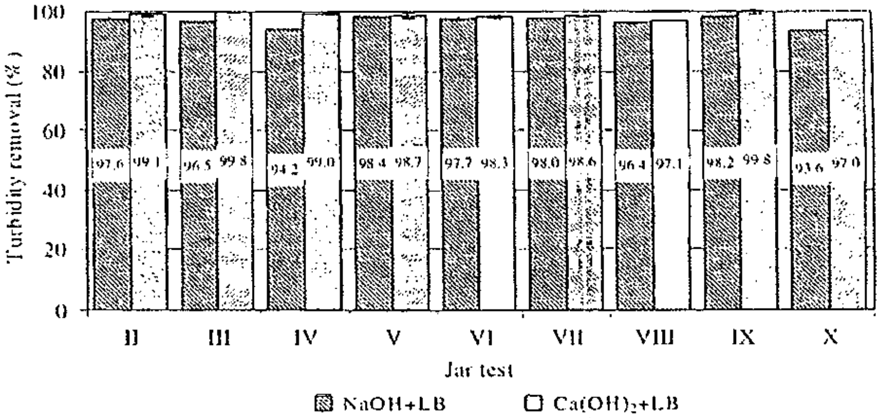

FIG. 4. Average Turbidity Removals by Alkalization-LB Treatment Process

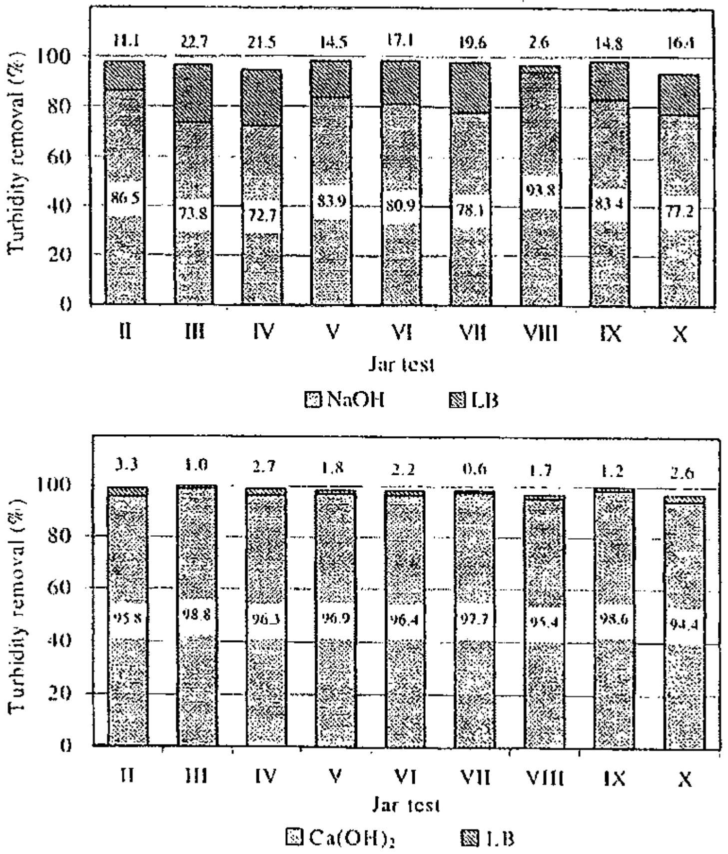

FIG. 5. Contribution of LB to Turbidity Removal in Alkalization-LB Treatment Process

the high ionic strength (4.05×10^{-2} salinity^{0}) (Wang and Chen 1983). The high magnesium content of LB induces $Mg(OH)_2$ floc formation to the greatest extent at a pH of 11.4 ± 0.1. The produced magnesium hydroxide is a gelatinous precipitate that has been found to serve as an efficient coagulant and also a flocculant aid (Vråle 1978). It has a large surface area and a positive surficial charge that attracts the negatively charged colloidal particles, including the $CaCO_3$ flocs, thus inducing adsorption and agglomeration (Elmaleh et al. 1996). Moreover, the high ionic strength of LB induces destabilization of colloids, as explained by the Gouy-Chapman theory, leading to higher removal efficiency (Wang and Chen 1983; Ødegaard 1989; Casey 1997).

It is also observed that the lime-magnesium process yields higher removals when compared to the caustic-soda-magnesium process. To capture the sole effect of LB contributing to turbidity removal, the data were processed and graphically presented in Fig. 5. It is noted that the addition of LB resulted in supplementary percent turbidity removals above alkalization, ranging from 2.6 to 22.7% for the caustic-soda-LB process and from 0.6 to 3.3% for the lime-LB process. It is obvious that the contribution of LB is greater in the former process because turbidity removals by caustic soda alkalization were lower than the lime alkalization process.

Total Metals

The removal patterns of eight metals from MWW were also assessed using alkalization or alkalization-LB treatment processes. The metals were individually added in jar test sets II–IX and concurrently in jar test set X.

Individually Added Metals. Varying degrees of metal removal were observed by alkalization alone. Each metal exhibited characteristic removal efficiency, which is probably attributed in relation to its hydroxide solubility properties (*The Merck* 1983) as well as affinity toward the precipitating suspended solids (Ødegaard 1989). Lime treated MWW samples showed higher metal removal efficiencies as compared to caustic soda treatment. Upon the addition of LB to the alkalized MWW samples, metal removal was enhanced significantly, especially with the NaOH alkalization process. Again, efficiency enhancement can be attributed to the enriched magnesium content as well as the high ionic strength of LB. Also, metal removal patterns were directly correlated with suspended solid removal patterns (Morgan and Stumm 1991). This is explained by the fact that metals are associated with suspended colloidal particles to a great extent but with varying affinities. Fig. 6 graphically compares average removal efficiencies for individually added metals after alkalization and after the alkalization-LB treatment processes.

Fig. 7 shows the contribution of LB to metal removal. It is noted that the addition of LB increased initial metal removal efficiencies by a range of 14.8–58.2% when MWW was alkalized with caustic soda and 1.6–23.2 when slaked lime was the alkalizing agent. Again, it is obvious that the contribution of LB is greater in the first process because initial metal removal efficiencies by the sole employment of caustic soda alkalization were lower than those attained in the lime alkalization process.

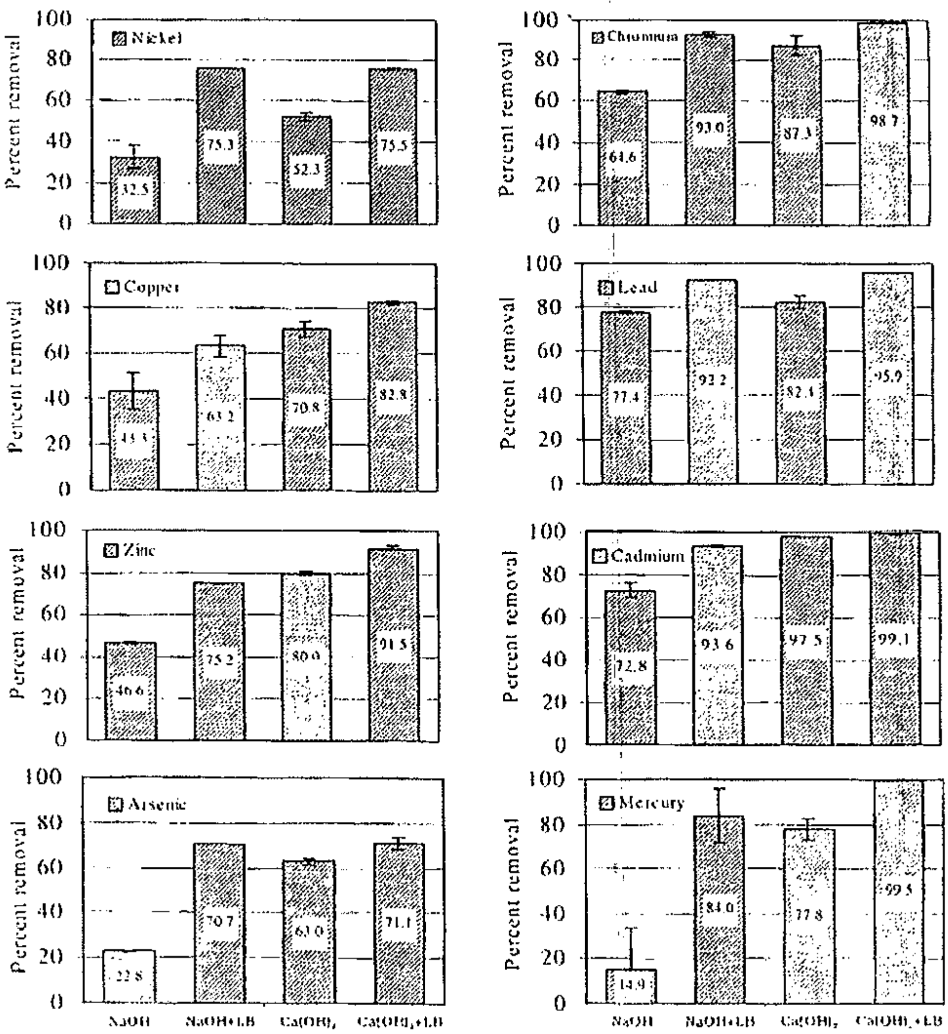

FIG. 6. Assessment of Removal Efficiencies for Various Individually Added Metals by Alkalization and Alkalization-LB Treatment Processes

Except for arsenic and nickel, the results indicate that metal removal percentages attained by the lime-LB process are very satisfactory (≥91.5% ± 1.0) (Table 6). Arsenic (III), the metal used in the tests, is known to exhibit low removal efficiencies compared to arsenic (V), which could be attributed to its negative charge in the pH range of 4–10 [Office of Groundwater and Drinking Water (OGDW) 1999]. To overcome this shortfall, As(III) may be converted to As(V) by oxidation prior to its treatment by the lime-LB process (USEPA 1999). Low percent copper removals may be attributed to the amphoteric nature of cupric hydroxide, which dissolves in concentrated alkaline solutions to form the soluble cuprate ions again. However, a more plausible reason for the low copper removals in this experiment is that cupric ions form a number of soluble copper complexes mostly with sulfate, carbonate, and sulfide ions (USEPA 1977). The formation of such soluble complexes seems to be induced by the addition of the sulfate-rich LB and by the sulfates normally present in wastewater. Edwards and Benjamin (1989) have stated that copper has the least affinity for ferrihydrite coating compared to cadmium and zinc complexes. Benjamin et al. (1996) also reported on typical removal efficiencies of soluble metals using coated sand to be 80% for Cu, 90% for Pb, and 98% for Cd, values that agree well with the results obtained in this study. As for nickel, low removal efficiencies are invariably reported in the literature for this metal. No plausible explanation has been presented as to the reasons leading to this behavior compared to most other metals of concern in wastewater treatment systems (Brown and Lester 1979; Patterson et al. 1981; Kodukula et al. 1994). A reasonable explanation may be the low affinity of nickel toward suspended solids in raw wastewaters as compared to other metals (Ødegaard 1989).

A comparison between the results obtained from this study and those reported by other studies (Table 7) indicates that the lime-LB process results in metal removal efficiencies that compare well to the results produced by other processes and for some metals surpass these results to achieve high removal levels.

Concurrently Added Metals. Six of the previously assessed eight metals were concurrently added to alkalized MWW samples. Selection was restricted to A-type nonvolatile metals: cadmium, chromium, copper, lead, nickel, and zinc. B-type semivolatile metals were not considered in this experiment. A comparison with the individually added metal removal percentages reveals that, regardless of the alkalization mode, the concurrent presence of metals does not induce a significant

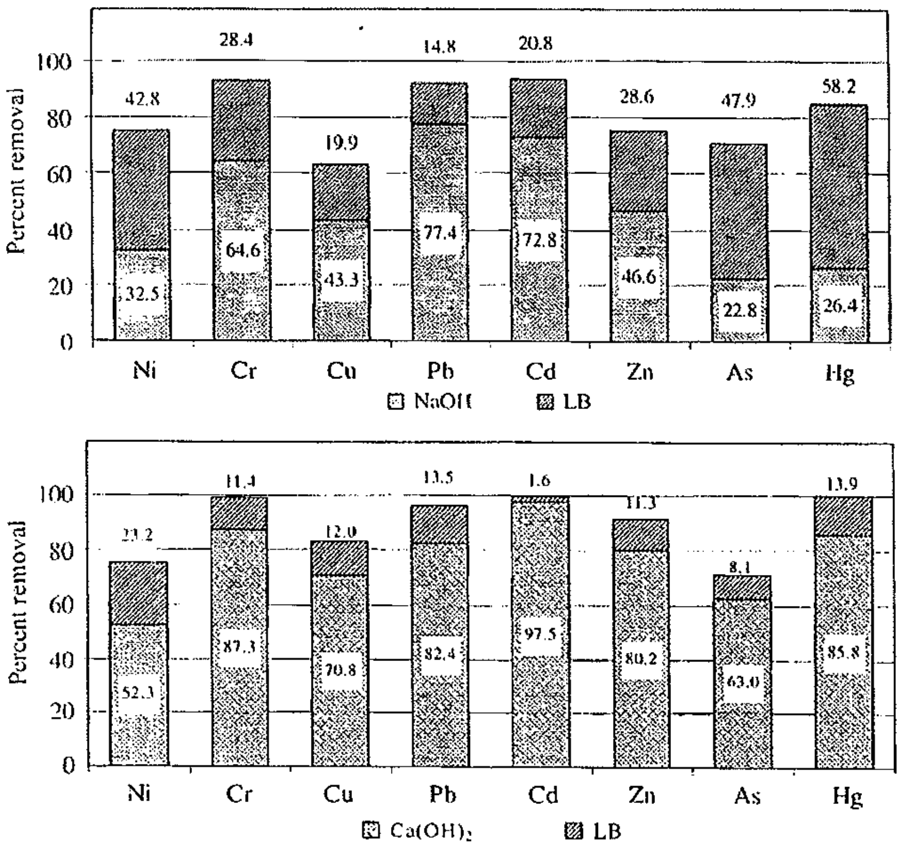

FIG. 7. Contribution of LB to Removal Efficiencies of Individually Added Metals

TABLE 6. Examples of Performance Standards for Direct Discharge[a]

Metal (1)	Effluent Standard (mg/L) Thailand (2)	KSA[b] (3)	Germany (4)	California[c] (5)
Ag	NR	NR	0.1	0.04
As	0.25	0.1	NR	0.02
Ba	1.0	NR	2.0	NR
Cd	0.03	0.02	0.005	0.03
Cr	0.5	0.1	0.5	0.01
Cu	1.0	0.2	0.3	0.3
Hg	0.005	0.001	0.005	0.002
Mn	5.0	NR	0.5 as $MnSO_4$	NR
Ni	0.2	0.2	0.5	0.2
Pb	0.2	0.1	0.1	0.2
Se	0.2	NR	NR	NR
Zn	5.0	1.0	0.5	0.5

Note: NR = not reported.

[a] Performance standards for direct discharge apply to sanitary sewage, surface runoff (including fire control waters), cooling water discharge, boiler water conditioning blowdown, process wastewaters and any other wastewater. Data condensed from Abu-Rizaiza (1999); Chen and Hendricks (1974); and (http://pcd.go.th/regulations).

[b] KSA = Kingdom of Saudi Arabia (1989).

[c] California state less than or equal to 10% effluent standards.

TABLE 7. Comparison of Metal Removals by Various Chemical Treatment Technologies

Metal (1)	Lime + LB[a] (2)	$FeCl_3$ + polymer + seawater[b] (3)	$FeCl_3$ + polymer[c] (4)	Chemical precipitation[d] (5)
Pb	95.9	64	33	>82
Cd	99.1	57	43	96
Cu	82.8	81	61	>99
Cr	98.7	83	71	NR
Hg	99.5	50	50	NR
Ni	75.5	70	26	98
Zn	91.5	50	57	93.7

[a] Data obtained from current study. Influent metal concentrations are 1 mg/L for every metal.

[b] Data from Oslo (VEAS) treatment plant (Odegaard 1992). Influent metal concentrations range from 0.7 to 121 μg/L.

[c] Data from the Hyperion treatment facility in Los Angeles (Harleman and Morrissey 1990). Influent metal concentrations are not reported. Facility receives MWW only; thus, metal concentrations are assumed to be minimal.

[d] Reported in USEPA's Risk Reduction Engineering Library (RREL) treatability database, version 5.0. Influent metal concentrations range from 0.1 to 1 mg/L for every metal. Exact type of chemical precipitation was not specified. Maximum reported values are considered in this table (Patterson et al. 1998).

hindrance effect except for nickel, as depicted in Fig. 8. In fact in the lime-LB treatment process, the percent removal of nickel increased by 18.5% when the metal was present concurrently with other metals.

All reported percentages are the averages of triplicate jar experiments. Mean analytical data of individual jar test sets are summarized in Tables 8 and 9.

Varying Concentrations of Metals. To evaluate the impact of metal removal efficiencies in relation to increasing initial concentrations of metals, gradually increasing doses of

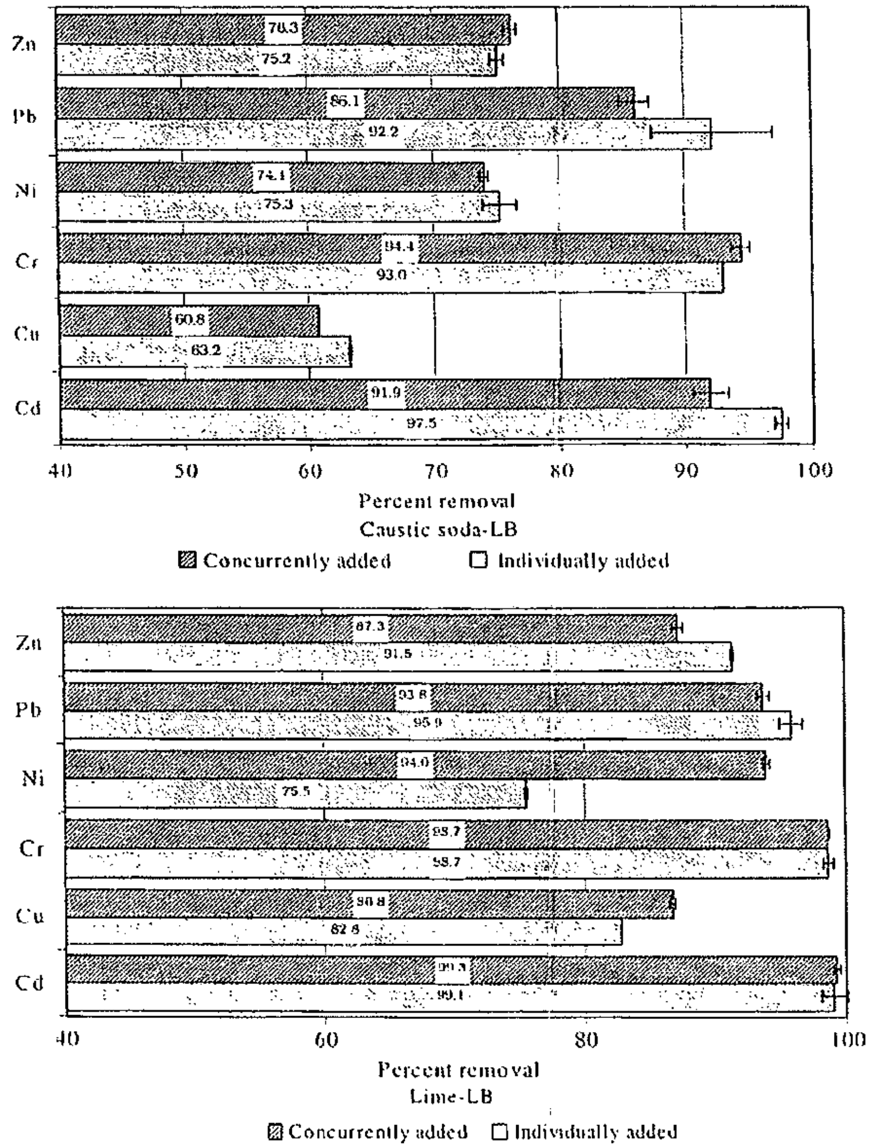

FIG. 8. Comparison of Individually and Concurrently Added Metal Removal Patterns by Alkalization-LB Processes

nickel were added to the experimental matrix. Nickel was selected because it exhibited lower average removal percentages in the presence of LB. Thus, volumes of 1, 2, 4, and 6 mL from the stock nickel solution were dispensed into alkalized 1-L aliquots of MWW to achieve nickel concentrations of 1, 2, 4, and 6 mg/L. Fig. 9 displays the attained metal removal percentages as a function of the added nickel concentration.

It can be deduced that metal removal percentages incrementally increase in relation to increasing influent concentrations of metals. Several investigators have reported the concentration dependence of metals removal data, which implies that higher influent concentrations result in greater metal removals (USEPA 1977; Esmond et al. 1980; Petrasek and Kugelman 1983).

CONCLUSIONS AND RECOMMENDATIONS

The present study demonstrates the effectiveness of LB in the removal of various metals from alkalized wastewater. Based on the outcomes of the performed study, the following conclusions can be drawn:

- Regardless of the alkalization mode adopted in this study, the optimum dose of magnesium ions for the magnesium-free suspension was about 134 mg/L. In the case of MWW, the magnesium salts present in LB proved to be most effective when applied at a dose of 107 mg/L after alkalizing the matrix with caustic soda or slaked lime.
- The enriched magnesium content and the high ionic strength that are the characteristics of LB contribute to its effectiveness as a coagulant.
- In the case of MWW, average metal removal percentages varied between 63.2% ± 4.7 and 93.6% ± 0.6 for the caustic-soda–LB process and 71.1% ± 2.7 and 99.5% ± 0.1 for the lime-LB process. Average metal removal efficiencies were signficantly lower by the sole employment of alkalization.
- The concurrent presence of metals in a given matrix in-

TABLE 8. Mean Analytical Data of Jar Test Sets II–IX for Individually Added Metals

Jar test (metal) (1)	Jar number (2)	Alkalizing agent (3)	Concentration of added LB (mg/L) (4)	Weight of added metal (μg) (5)	pH (6)	Turbidity (NTU) (7)	EC (μmhos/cm) (8)	TDS (mg/L) (9)	Recovered weight of metal[a] (μg) (10)
II (Ni)	J1	None	0	0	7.74	108.3	1,844.4	923.1	36.0 ± 0.0
	J2	None	0	1,000	7.66	114.1	1,858.4	928.4	1,050.0 ± 0.0
	J3	NaOH	0	1,000	10.75	14.5	2,909.2	1,446.7	674.7 ± 53.2
	J4	NaOH	107	1,000	10.31	2.6	3,844.2	1,930.0	246.7 ± 0.0
	J5	Ca(OH)$_2$	0	1,000	10.89	4.5	1,959.2	967.9	476.9 ± 19.6
	J6	Ca(OH)$_2$	107	1,000	10.17	0.9	2,980.0	1,490.0	244.7 ± 3.9
III (Cr)	J1	None	0	0	7.74	210.0	1,434.8	717.8	3.71 ± 1.0
	J2	None	0	1,000	7.35	222.5	1,460.5	730.8	978.3 ± 19.8
	J3	NaOH	0	1,000	10.78	55.0	2,240.0	1,118.3	354.0 ± 10.6
	J4	NaOH	107	1,000	10.42	7.4	3,254.2	1,630	70.2 ± 13.3
	J5	Ca(OH)$_2$	0	1,000	11.01	2.6	1,631.3	732.3	127.1 ± 49.2
	J6	Ca(OH)$_2$	107	1,000	10.30	0.5	2,471.7	1,235.8	12.6 ± 1.1
IV (Cu)	J1	None	0	0	7.91	95.3	1,462.2	731.6	16.8 ± 1.0
	J2	None	0	1,000	7.88	96.8	1,452.2	725.8	1,002.6 ± 0.5
	J3	NaOH	0	1,000	10.91	25.8	2,470.8	1,238.3	566.7 ± 80.9
	J4	NaOH	107	1,000	10.54	5.5	3,018.3	1,509.2	368.1 ± 47.4
	J5	Ca(OH)$_2$	0	1,000	11.06	3.6	1,605.4	801.9	292.2 ± 36.6
	J6	Ca(OH)$_2$	107	1,000	10.54	0.9	2,094.4	1,048.1	171.7 ± 9.1
V (Pb)	J1	None	0	0	7.85	78.4	1,446.3	724	15.8 ± 2.2
	J2	None	0	1,000	7.50	77.4	1,473.4	736.2	992.2 ± 4.2
	J3	NaOH	0	1,000	11.2	12.6	3,168.3	1,582.5	225.9 ± 5.8
	J4	NaOH	107	1,000	10.6	1.3	3,592.5	1,798.3	78.5 ± 0.3
	J5	Ca(OH)$_2$	0	1,000	11.2	2.4	2,252.5	1,044.2	176.4 ± 30.1
	J6	Ca(OH)$_2$	107	1,000	10.48	1.1	2,607.5	1,305.8	41.2 ± 0.3
VI (Zn)	J1	None	0	0	7.75	131.2	1,424.7	712.8	461.3 ± 49.5
	J2	None	0	1,000	7.38	129.0	1,444.1	722.2	1,571.9 ± 53.6
	J3	NaOH	0	1,000	11.26	28.8	3,040.0	1,518.3	839.9 ± 21.3
	J4	NaOH	107	1,000	10.64	2.9	3,478.3	1,744.2	390.3 ± 6.2
	J5	Ca(OH)$_2$	0	1,000	11.43	3.0	2,818.3	1,408.3	314.5 ± 22.4
	J6	Ca(OH)$_2$	107	1,000	10.91	2.2	2,742.2	1,380.0	134.3 ± 20.7
VII (Cd)	J1	None	0	0	7.86	110.6	1,415.0	707.6	3.30 ± 0.0
	J2	None	0	1,000	7.47	109.6	1,433.8	709.1	868.0 ± 42.1
	J3	NaOH	0	1,000	11.19	21.1	2,704.2	1,370.8	271.5 ± 33.0
	J4	NaOH	107	1,000	10.54	2.2	3,449.2	1,728.3	64.4 ± 2.0
	J5	Ca(OH)$_2$	0	1,000	11.36	4.0	2,566.7	1,320.8	24.7 ± 0.4
	J6	Ca(OH)$_2$	107	1,000	10.83	1.5	2,775.8	1,381.7	8.7 ± 0.6
VIII (As)	J1	None	0	0	7.81	71.3	1,233.8	616.7	41.5 ± 2.0
	J2	None	0	1,000	7.46	68.1	1,245.4	622.9	893.3 ± 2.6
	J3	NaOH	0	1,000	11.29	4.4	2,627.5	1,316.7	772.4 ± 1.1
	J4	NaOH	107	1,000	10.64	2.6	3,305.8	1,655.8	292.8 ± 3.1
	J5	Ca(OH)$_2$	0	1,000	11.23	3.3	1,499.7	746.6	370.1 ± 15.2
	J6	Ca(OH)$_2$	107	1,000	10.72	2.0	2,342.5	1,174.2	288.7 ± 27.4
IX (Hg)	J1	None	0	0	8.12	97.0	1,973.6	988.0	3.7 ± 2.9
	J2	None	0	1,000	7.93	95.0	1,986.6	993.6	1,000.0 ± 118.0
	J3	NaOH	0	1,000	11.14	16.1	3,380.8	1,688.3	851.4 ± 185.6
	J4	NaOH	107	1,000	10.70	1.7	4,323.3	2,166.7	160.5 ± 121.6
	J5	Ca(OH)$_2$	0	1,000	11.41	1.3	1,724.1	859.5	222.2 ± 49.5
	J6	Ca(OH)$_2$	107	1,000	10.51	0.2	3,120.8	1,562.5	5.1 ± 1.0

[a] Average weight of recovered metal ± standard deviation of triplicate jar tests.

TABLE 9. Mean Analytical Data of Jar Test Set X for Concurrently Added Metals

Parameter (1)	Jar Number					
	J1 (2)	J2 (3)	J3 (4)	J4 (5)	J5 (6)	J6 (7)
Alkalizing agent	None	None	NaOH	NaOH	Ca(OH)$_2$	Ca(OH)$_2$
Concentration of added LB (mg/L)	0	0	0	107	0	107
Weight of added metal (μg)	0	1,000	1,000	1,000	1,000	1,000
pH	8.06	6.98	10.96	10.57	11.79	11.11
Turbidity (NTU)	67.00	87.25	15.32	4.24	3.68	2.02
TDS (mg/L)	1,190.0	1,254.2	1,825.8	2,312.5	1,823.3	1,798.3
EC (μmhos/cm)	2,364.2	2,504.2	3,643.3	4,612.5	3,621.7	3,600.8
Recovered weight of metal[a] (μg)						
Ni	10.9 ± 5.9	1,052.9 ± 3.6	507.6 ± 39.7	273.1 ± 9.1	111.2 ± 21.6	63.1 ± 1.3
Cr	1.7 ± 0.1	1,004.0 ± 5.2	611.7 ± 36.4	56.0 ± 3.6	22.8 ± 3.1	13.5 ± 2.7
Cu	14.8 ± 0.9	1,078.3 ± 17.1	603.6 ± 4.8	422.9 ± 6.0	207.8 ± 5.9	141.9 ± 2.9
Pb	32.8 ± 2.3	1,063.1 ± 16.7	233.5 ± 15.8	147.6 ± 2.3	312.7 ± 20.8	66.3 ± 3.7
Cd	5.9 ± 2.0	901.6 ± 30.2	177.8 ± 0.5	72.9 ± 7.1	11.7 ± 6.1	6.2 ± 3.4
Zn	480.7 ± 0.0	1,483.0 ± 13.5	415.1 ± 24.1	351.5 ± 17.4	347.6 ± 30.9	188.3 ± 5.8

[a] Average weight of recovered metal ± standard deviation of triplicate jar tests.

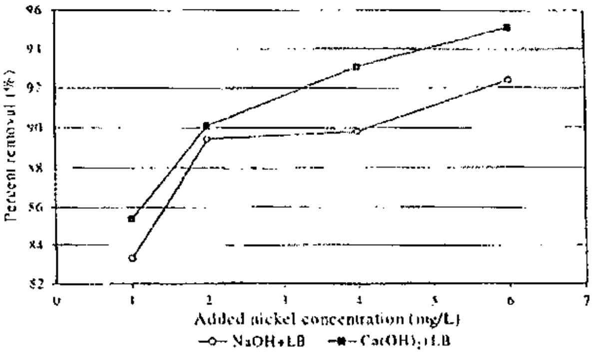

FIG. 9. Nickel Removal Percentages as Function of Added Metal Concentration

duced varying effects on attained metal removal efficiencies. In the case of MWW, no significant change was observed in metal removal efficiencies when compared to individually added metal removal patterns. Remarkably with this matrix, nickel removal increased by the lime-LB process when the metal was present concurrently with other metals.

- Metal removal patterns demonstrated concentration dependence, which implies that higher influent metal concentrations result in greater metal removals. Nickel removal percentages incrementally increased in relation to increasing influent concentrations of the metal. Attained efficiencies for the caustic-soda–LB process were 83.3, 89.4, 89.8, and 92.4% for an initial nickel concentration of 1, 2, 4, and 6 mg/L, respectively. On the other hand, the lime-LB process yielded nickel removals of 85.4, 90.1, 93.1, and 95.1%, respectively.
- Upon the addition of LB, the pH levels of the alkalized experimental matrices decreased by an average of 4.5% for the caustic-soda–LB process and 5.8% for the lime-LB process. Consequently, lower dosages of carbon dioxide are needed to decrease the effluent pH to acceptable levels as compared to high lime (pH > 11) treatment processes.
- The lime-LB process proved to be a more effective treatment process than the caustic-soda–LB process in terms of enhanced heavy metal as well as turbidity removals and lower effluent pH.
- Heavy metal removal by the alkalization-LB process is complimentary to the previously demonstrated efficiency of LB in removing TSS, COD, nutrients, and color.

Based on the above conclusions, the following recommendations are proposed:

- Apply the proposed chemical wastewater treatment scheme in coastal communities where LB can easily be obtained as the by-product of seawater solar evaporation, commonly used to produce table salt.
- Carry out further research to investigate the effectiveness of the alkalization-LB process in the removal of heavy metals from various industrial wastewaters. Originally, alkaline industrial effluents may require the sole addition of LB to attain high metal removal efficiencies.
- Carry out further research to examine the effectiveness of the alkalization-LB process in the removal of heavy metals existing in various combinations and varying in initial concentrations.

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