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Pollution Assessment and Mining at Jazan Coastline, Saudi Arabia

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Abstract

The present work aims to evaluate and document the heavy metal distribution along Jazan coastline, southwest Saudi Arabia. Moreover, a trial for mining minerals from seawater has been performed where solvent extraction of a spike solution containing copper, cobalt and nickel has been investigated to attain the optimal extraction conditions. The optimum conditions are found to be 7 M hydrochloric acid concentration, 5 M $[H^+]$ for 3 min shaking time with Cyanex 923 solvent conc. of 0.1 M (1:1 aqueous/organic phase ratio) at temp. 25˚C. These conditions realized 92.5% copper extraction as well as 95.6% and 96.2% for cobalt and nickel extraction respectively.

Keywords

Heavy Metals, Assessment, Solvent Extraction, Mining from Sea Water

1. Background

Coastal environments are subjected to heavy metals pollution due to population and industrial activities. Coastal areas are considered as monitoring sites for environmental pollution worldwide, so many studies have been achieved to assess coastal pollution. Most of the previous studies used coastal sediments as Abrahim and Parker [1], Diaz-de Alba *et al.* [2] and Hahladak *et al.* [3]. Almasoud *et al.* [4] concluded enrichment of zinc, copper, chromium and lead of anthropogenic sources along the Arabian Gulf Coast. Yousef *et al.* [5] reported high arsenic and mercury concentrations along Turut Island Coast due to landfilling and oil pollution. Nour and Elsorogy [6] concluded enrichment of Pb, Ni, Cd, Co, Cu and Zn on the Sabratha Coastline, Libya due to different anthropogenic activities.

Alharbi *et al.* [7] studied the distribution of heavy metals along Al khobar coast, Arabian Gulf of Saudi Arabia to identify the sources of pollution and compare with other neighboring worldwide coasts. This evaluation helps the coastal strategies for better management of the coastal activities where the Arabian Gulf is one of the important marine waterways that include a lot of commercial and industrial activities.

El Sorogy *et al.* [8] studied the distribution of heavy metals along Dammam coastal area, Saudi Arabian Gulf to evaluate the human activities and compare the rate of pollution in Dammam coastline with other neighboring worldwide coasts. The most recorded pollutants were sewage effluents, landfilling due to coastal infrastructural development, oil spills, petrochemical industries and desalination plants.

On the other hand, population and industry rapid growth have increased the demand for clean water, which necessitates the presence of many seawater desalination plants. The desalination cost will fall if additional income generated from seawater mining (recovery of valuable minerals). As well as the developing countries can afford fertilizers containing plant nutrients (Mg-K-Ca-S) through seawater mining. Moreover, seawater mining is advantageous as high grade minerals on land mining are depleting leaving low grade minerals, so increase the cost. Also, land mining results in environmental problems and hazards to miners Paripurnanda *et al.* [9], however, the advantage of seawater mining is that seawater is homogenous and there is no mineral grades difference as on land mining. There is a great demand for using these minerals in industry, agriculture, environmental remediation and medicine (**Table 1**).

Generally, there are four methods often used for mining from seawater; solar evaporation, electro-dialysis ED,u membrane distillation/crystallization MD/MDC and adsorption/desorption/crystallization. The latter technique will be applied in this paper where solvent is applied to recover copper, cobalt and nickel. Shinde and Dhadke [10], studied the solvent extraction separation of copper and nickel

Table 1. Seawater minerals and their uses.

Mineral	Uses
Na (NaCl, Na_2CO_3, Na_2SO_4)	Food, soap, detergents, glass and paper industries, road de-icing
Mg (Mg, $MgCO_3$, $MgSO_4$)	Chemical and construction industries, fertilizers
Ca ($CaCO_3$, $CaSO_4$)	Construction industries, fertilizers
K (KCl, K_2SO_4)	fertilizers
Br	Fire retardant, petroleum additives
B	Glass, soap, fertilizers, detergent, fire retardant
Sr	Ceramics, glass, fireworks, phosphorescent lights and pigments
Li	Batteries, glass, lubricants
Rb	Fibre optics, lamps
U	Nuclear fuel in nuclear power reactor

by Cyanex 301. Shamsul Baharin Jamaludin [11], investigated the extraction of copper, nickel and zinc from their sulphate solutions using [bis(2,4,4-trimethyl pentyl) phosphinic acid] (Cyanex 272, HA) as an extractant. Moreover, Sadat *et al.*, [12], studied the Separation of Cu from dilute Cu-Ni-Co bearing bioleach solutions using solvent extraction with Chemorex CP-150.

The present work aims to determine the heavy metals distribution along Jazan coastline, southwest Saudi Arabia. Moreover, a trial for mining minerals from seawater, solvent extraction of a spike solution containing copper, cobalt and nickel has been investigated to attain the optimum extraction conditions.

2. Experimental

2.1. Samples

The study area, Jazan, is located along the red sea coast at southwest of Saudi Arabia Kingdom. In order to assess the heavy metal distribution along Jazan coastline, 15 seawater, 10 seaweeds and 15 sediments samples (at 5 to 30 cm depth) were collected and analyzed for its heavy metal concentration Li, Be, V, Mg, Mn, Co, Ni, Cu, Rb, As, Se, Sr, Cd, Pb and U using Inductively Coupled Plasma Mass Spectrometer (ICP-MS): Nex1ON 300 D (Perkin Elmer, USA) at Jazan University. Total dissolved solids (TDS), pH and electrical conductivity (EC) were directly measured. A closed microwave system, CEM MDS-2000 (USA) was used for wet digestion of sediments samples.

2.2. Reagents

Seawater and sediment samples are divided into three main groups (from 3 localities); Group (1) includes samples 1 to 5, Group (2) includes samples 6 to 10 while Group (3) includes samples 11 to 15. Spike solution consists of copper, cobalt and nickel chlorides (Merck, AR grade) was prepared by dissolving the required amounts in double-distilled water. One ml of concentrated HCl was added to the solution to avoid further hydrolysis. The commercial extractant, Cyanex 923, obtained from Cytec Inc. of Canada, was used. Kerosene was used as organic phase diluent. All other reagents used were of analytical reagent grade.

2.3. Extraction Procedure

Solvent extraction of a spike solution containing copper, cobalt and nickel has been carried out from 1 M chloride solution using Cyanex 923 diluted with kerosene. Equal aliquots (10 ml) of the aqueous phase and the organic phase were shaken for 10 minutes in a separating funnel. The phases were allowed to settle for 10 minutes then separated. The concentration of elements in the aqueous phase before and after the extraction was determined using an atomic absorption spectrophotometer, then the percentage of extraction has been calculated. The relevant factors affecting the extraction as pH, extractant concentration, metal ions concentration, time, temperature as well as O/A phase ratio have been studied and optimized.

3. Results and Discussions

3.1. Heavy Metals Assessment at Jazan Coastline

Physical properties of seawater and sediments samples of Jazan coastline as well as heavy metal concentration of all samples are shown in Table 2.

From the resulted data, it is clear that pH ranges from 7.40 (sample no. 14) to 8.10 (sample no. 1, 8 and 16). Whereas EC of seawater ranges from 68.180 (sample no. 6) to 73.800 µs/cm (sample no. 1). Finally, TDS ranges from 46.450 to 55.680 mg/L (samples 14 and 4 respectively).

The data summarized in Table 3, Table 4 and Figure 1, Figure 2, showed that the distribution of Cd in seawater samples varied from 114 µg/L in samples no. 4 and 6 to 130 µg/L in samples no. 11 and 12 while in sediment samples ranged from 38 µg/g in sample no. 1 to 80 µg/g in sample no. 8. Moreover, Pb in seawater samples varied from 123 to 199 µg/L while in sediments samples ranged from 90 to 148 µg/g. In the meantime, Cu in seawater samples varied from 360 to 404 µg/L while in sediments samples ranged from 68 to 890 µg/L. As in seawater samples varied from 30 to 110 µg/L while in sediments samples ranged from 34 to 66 µg/L. Finally, Co and Ni in seawater samples varied from 48 and 52 µg/L to 92 and 120 µg/L respectively while in sediments samples ranged from 40 and 90 µg/g to 64 and 220 µg/g respectively.

In other words; seawater samples are divided into three main groups; Group 1 includes samples 1 to 5 that recorded the lowest values of V, Mn, Pb and highest values of Co and As, Group 2 includes samples 6 to 10 that recorded the lowest values of Be, Co and highest values of Ni, V while Group 3 includes samples 11 to 15 that recorded the lowest values of Co, As and highest values of Be, Mn, Cu, Cd, Se and Pb.

Table 2. Physical properties of seawater and sediments samples of Jazan coastline.

Sample No.	pH	EC	TDS	Sample No.	pH	EC	TDS
1	8.10	73.800	55.600	16	8.10	73.690	55.660
2	7.88	69.800	47.000	17	7.88	69.800	47.000
3	7.94	69.960	47.400	18	7.94	69.960	47.400
4	8.00	70.400	55.680	19	8.05	72.400	55.680
5	8.00	70.120	55.080	20	8.05	72.600	55.000
6	7.60	68.180	55.280	21	8.00	70.180	55.660
7	7.86	69.760	46.800	22	7.82	68.700	46.500
8	8.10	71.100	55.080	23	8.05	71.120	55.080
9	7.88	69.820	47.000	24	7.42	69.680	46.460
10	7.90	69.780	47.320	25	7.98	69.960	48.000
11	7.46	70.400	55.680	26	8.00	70.400	55.680
12	8.05	71.380	55.260	27	8.05	71.080	54.920
13	8.05	71.390	55.280	28	8.05	70.990	55.280
14	7.40	69.680	46.450	29	7.84	68.750	47.000
15	8.00	70.080	54.800	30	8.00	70.080	54.800

Table 3. Metal conc. in seawater samples of Jazan coastline (μg/L).

Samp. no.	Li	Be	Mg	V	Mn	Co	Cu	As	Se	Rb	Sr	Ni	Cd	Pb	U
SW 1	218	71.8	104	82	115	92	360	110	1717	115	54	55	115	123	nd
SW 2	218	68.4	102	88.2	117	92	366	102	1770	116	56	56	117	128	nd
SW 3	216	70.2	105	87.6	114	91	362	100	1700	116	54	56	116	130	nd
SW 4	228	68.8	105	88.2	118	90	368	100	1720	114	54	58	114	133	nd
SW 5	222	69.2	104	84.8	118	90	366	102	1700	116	52	52	117	128	nd
SW 6	230	39.5	109	104	203	49	370	95	1773	112	54	120	114	173	nd
SW 7	240	40.2	107	102	206	49	374	90	1800	116	55	118	117	177	nd
SW 8	230	39.8	103	106	203	49	370	94	1820	115	54	100	118	174	nd
SW 9	237	38	109	108	208	48	376	94	1780	116	56	116	118	174	nd
SW 10	244	39.8	110	104	206	49	376	98	1760	118	55	104	116	178	nd
SW 11	232	103	110	96.5	219	49	404	30	2054	113	54	58	130	194	nd
SW 12	230	105	104	100	218	48	404	48	2020	110	56	58	130	199	nd
SW 13	238	108	103	96.4	217	52	400	44	2030	102	58	54	128	192	nd
SW 14	232	100	110	100	218	49	400	48	2050	100	57	57	128	192	nd
SW 15	240	102	110	98.2	216	52	404	38	2040	110	55	55	118	198	nd
Min	218	38	102	82	114	48	360	30	1700	100	52	52	114	123	nd
Max	244	108	110	108	218	92	404	110	2054	118	58	120	130	199	nd
Average	231	63	106	95	166	70	382	70	1877	109	55	86	122	161	nd

Table 4. Metal conc. in sediments samples of Jazan coastline (μg/g).

Sample no.	Li	Be	Mg	V	Mn	Co	Cu	As	Se	Rb	Sr	Ni	Cd	Pb	U
S 1	33	880	33	80	125	46	838	34	458	32	55	105	38	128	203
S 2	38	820	39	104	160	48	840	39	560	39	65	98	50	120	320
S 3	40	850	38	105	160	48	840	43	565	45	65	90	50	110	340
S 4	44	620	224	43	33	64	890	42	440	82	135	106	60	118	463
S 5	37	690	222	49	44	44	880	38	422	44	144	120	50	110	490
S 6	31	680	30	50	39	63	86	34	404	30	240	130	53	115	525
S 7	30	773	35	213	213	49	68	37	632	26	220	200	46	140	188
S 8	32	776	39	210	170	50	78	36	606	43	218	220	80	140	269
S 9	128	663	44	169	162	45	83	42	585	53	230	330	75	144	263
S 10	120	660	49	180	180	40	88	36	620	55	230	200	70	120	277
S 11	108	590	48	150	166	49	82	60	538	45	66	212	60	100	250
S 12	100	480	42	204	176	49	80	58	589	54	58	120	50	90	268
S 13	120	490	44	200	187	44	84	55	604	59	48	180	55	120	266
S 14	128	580	44	180	166	47	99	66	604	58	55	188	50	148	270
S 15	120	600	49	188	198	47	90	60	601	66	46	166	58	120	299
Min	30	620	30	43	33	40	68	34	404	30	46	90	38	90	188
Max	128	880	224	213	213	64	890	66	632	82	240	220	80	148	490
Average	79	750	127	128	123	52	479	50	518	56	143	155	59	119	339

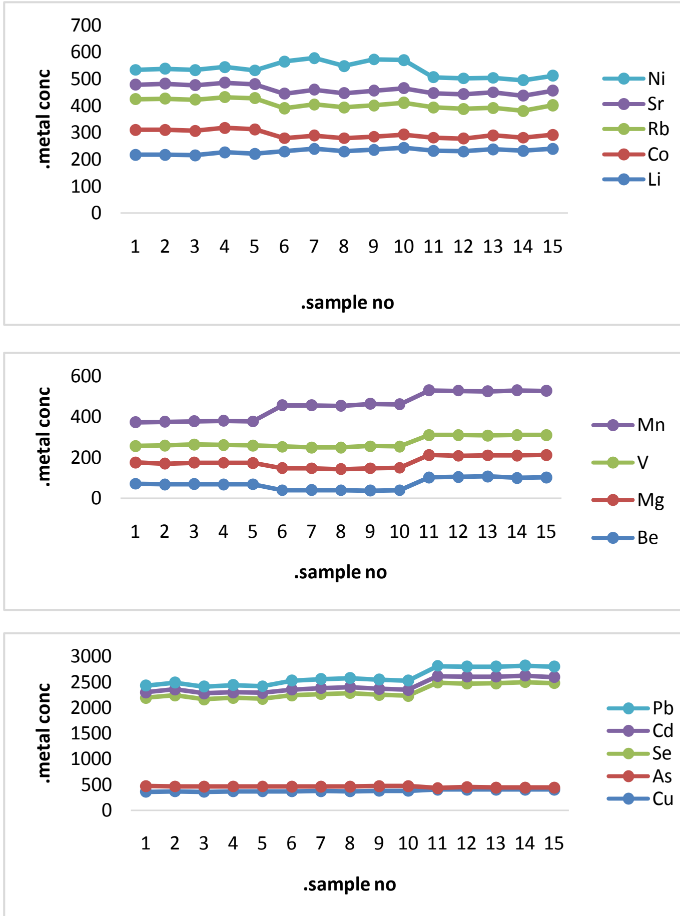

Figure 1. Metal conc. in seawater samples of Jazan coastline.

In the meantime, the average values of all heavy metals in seaweeds samples are recorded in Table 5 and Figure 3. Comparison of average values of Jazan sediments with other coasts worldwide is shown in Table 6, where the high As, Pb and Cd values may be attributed to industrial city of Jazan, desalination plants as well as fishing boats.

3.2. Solvent Extraction of Spike Seawater Solution

The extraction of copper, cobalt and nickel from spike 1 M chloride solution using Cyanex 923 as extractant diluted with kerosene was investigated. The effect of shaking time, acid concentration, extractant concentration, H^+ ion concentration and temperature on the extraction was studied.

3.2.1. Effect of Acid Concentration

The extraction of Cu, Co and Ni with 0.1 M Cyanex 923 in kerosene was studied by varying the HCl concentration from 1 M to 8 M. The extraction increased till 7 M HCl and then decreased. Data are shown in Table 7, Figure 4. The decrease may be attributed to the competition of HCl with metal species for solvent extraction.

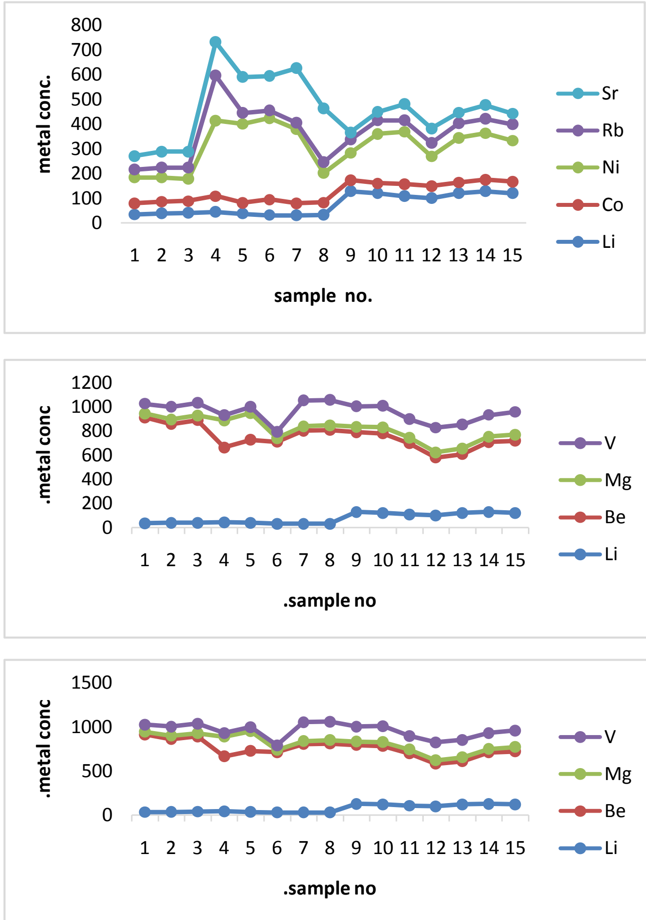

Figure 2. Metal conc. in sediments samples of Jazan coastline.

Table 5. Metal conc. in seaweeds samples of Jazan coastline (μg/g).

Samp. no.	Li	Be	Mg	V	Mn	Co	Cu	As	Se	Rb	Sr	Ni	Cd	Pb	U
1	178	965	260	268	64	108	1475	168	520	250	325	260	166	182	295
2	178	966	250	278	60	106	1478	163	400	250	285	240	160	182	290
3	158	880	256	290	58	114	1388	160	500	230	330	180	180	190	285
4	166	888	200	330	59	158	1400	164	680	236	280	188	190	160	285
5	158	900	220	330	50	160	1380	164	480	252	288	210	140	110	288
6	160	940	234	269	60	180	1400	160	622	240	290	230	240	120	290
Min	158	880	200	268	50	106	1380	160	400	230	280	180	160	110	285
Max	178	966	260	330	64	180	1478	168	680	252	330	260	240	190	295
Average	168	923	220	299	57	143	1429	164	540	241	305	220	200	150	290

3.2.2. Effect of Time

The effect of time on the extraction of Cu, Co and Ni from 5 M HCl with 0.1 M Cyanex 923 in kerosene at 1:1 phase ratio was investigated. As the time increase, the extraction increased and then decreased. The equilibrium is achieved in only 3 min. So, in all experiments, three minutes shaking time was maintained. Data are in Table 8, plotted in Figure 5.

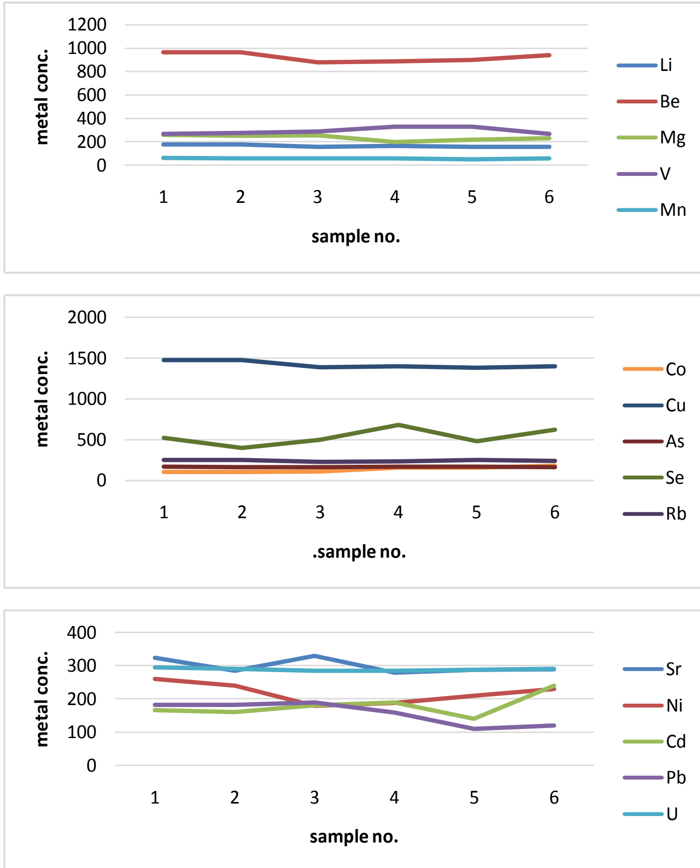

Figure 3. Metal conc. in seaweeds samples of Jazan coastline.

Table 6. Comparison between metals conc. of Jazan sediments and other worldwide localities (after El-Sorogy *et al.*, 2018) (μg/g).

location	Li	Be	Mg	V	Mn	Co	Cu	As	Se	Rb	Sr	Ni	Cd	Pb	U
Jazan, Red Sea, KSA	79	750	127	128	123	52	479	50	518	56	143	155	59	119	339
Arabian Gulf, Dammam KSA,	--	--	--	603	111.57	4.01	297.29	30.61	--	--	4801.7	77.1	2.13	5.25	--
Tarut Island					11.9 - 243.9	1.8 - 12	1.4 - 21	53 - 342	0.1 - 0.9				0.1 - 3.5	5.2 - 471	
Arabian Gulf, Khobar, KSA	--	--	--	268	113.97	4.75	182.97	1.606	--	--	1568	75.10	0.226	5.358	--
Gulf of Aqaba	--	--	--	--	--	0.77	10.8	15.1	--	--	--	--	0.07	6.8	--
Mediterran. Sea, Libya	--	--	--	--	36.21	5.95	17.30	--	--	--	--	22.65	0.83	11.69	--
Mediterran. Sea, Egypt	--	--	--	374.8	553	69.8	24.6	298.2	--	--	114.06	480.86	28.88	384.68	--
Salaam Coast, Tanzania	--	--	--	13	219	2.75	2.1	1.3	--	--	--	2.9	0.4	2.2	--

3.2.3. Effect of Solvent Concentration

The extraction of Cu, Co and Ni from 5 M HCl solution with 0.1 M to 1 M Cyanex 923 in kerosene was investigated. The extraction increased with increasing the solvent concentration as shown in Table 9, Figure 6.

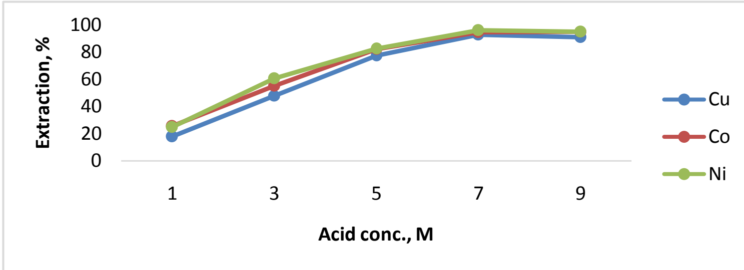

Figure 4. Effect of acid conc. on the metal extraction from spike seawater solution.

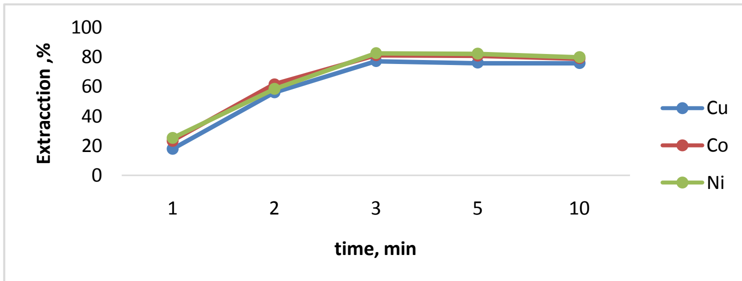

Figure 5. Effect of time on the metal extraction from spike seawater solution.

Table 7. Effect of acid conc. on the metal extraction.

Acid conc., M	Extraction Efficiency, %		
	Cu	Co	Ni
1	17.8	25.5	24.7
3	47.9	55.2	60.5
5	77.2	82.2	82.4
7	92.5	94.6	96.0
9	90.7	95.0	94.8

Table 8. Effect of time on the metal extraction.

Time, min	Extraction Efficiency, %		
	Cu	Co	Ni
1	17.9	23.4	25.2
2	56.2	61.6	58.5
3	77.2	81.2	82.5
5	76	80.8	82.0
10	75.8	79.0	79.8

3.2.4. Effect of Hydrogen Ion Concentration

The effect of hydrogen ion concentration on the extraction of Cu, Co and Ni with 0.1 M Cyanex 923 and 7 M chloride ion concentration was studied. The copper extraction increased from 84.5% to 92.5% with increasing the hydrogen ion concentration from 1 to 5 M. Other data are shown in Table 10, Figure 7.

Table 9. Effect of solvent conc. on the metal extraction.

Solvent conc., M	Extraction Efficiency, %		
	Cu	Co	Ni
0.1	77.2	84.4	85.2
0.3	82.2	88.5	90.2
0.5	88.5	96.0	94.0
1	96.8	97.0	97.4

Table 10. Effect of [H⁺] on the metal extraction.

$[H^+]$	Extraction Efficiency, %		
	Cu	Co	Ni
1	84.5	86.8	87.2
3	89.0	93.5	94.2
5	92.5	95.6	96.2
7	91.0	92.0	94.5

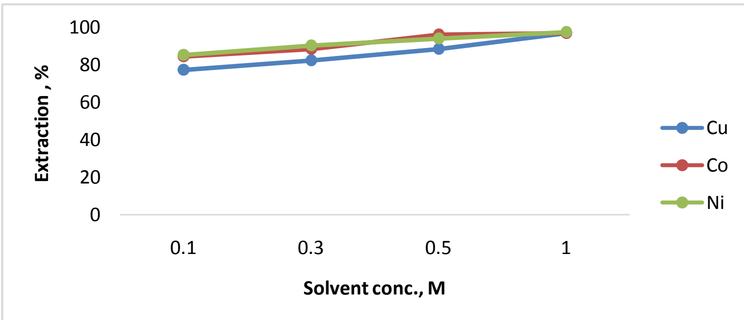

Figure 6. Effect of solvent conc. on the metal extraction from spike seawater solution.

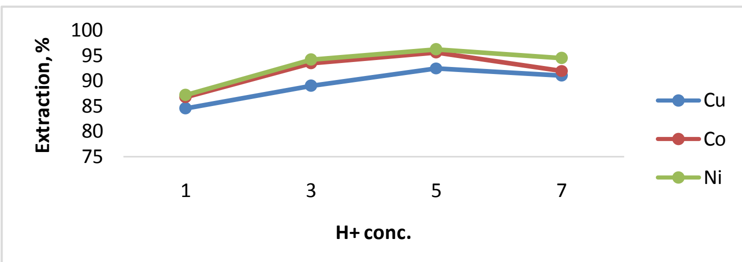

Figure 7. Effect of $[H^+]$ on the metal extraction from spike seawater solution.

3.2.5. Effect of Temperature

The effect of temperature on the extraction of Cu, Co and Ni from 5 M HCl, 7 M hydrogen ion conc. with 0.1 M Cyanex 923 at 1:1 phase ratio was studied from 20˚C to 40˚C. Extraction of all metal ions increased till 35˚C then decreased.

4. Conclusions

From the overgoing study of the heavy elements distribution along Jazan coastline, it is showed that no contamination except for arsenic, cadmium and lead that may be attributed to Jazan new industrial city, desalination plants, sewage effluent and fishing boats.

Moreover, solvent extraction of a spike seawater solution containing copper, cobalt and nickel has been investigated and the optimum extraction conditions are 7 M hydrochloric acid concentration, 5 M $[H^+]$ for 3 min time with Cyanex 923 solvent conc. of 0.1 M (1:1 Phase ratio) at temp. 25˚C. These conditions realized 92.5% copper extraction as well as 95.6% and 96.2% cobalt and nickel extraction respectively.

Thus in desert countries like Saudi Arabia, where fresh water is less potable, the desalination cost will fall down if additional income generated from seawater mining (recovery of valuable minerals). At the same time, mineral resources are preserved for the future generations.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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