SEBHA UNIVERSITY JOURNAL OF PURE & APPLIED SCIENCES VOL.21 NO. 2 2022
DOI: 10.51984/JOPAS.V21I2.2046

مجلة جامعة سبها للعلوم البحتة والتطبيقية
Sebha University Journal of Pure & Applied Sciences

Journal homepage: www.sebhau.edu.ly/journal/index.php/jopas

Treatment of Heavy Metals in Water Accompanied with Oil and A Soil Using some Expired Drugs at Al-Wahat/ Libya

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Keywords:
Heavy metals
Expired drugs
Water accompanied with oil
Soil
Water treatment

ABSTRACT

Heavy metals associated with oil production sites are the main contamination source for surrounding environments and groundwater. Groundwater contamination with such heavy metals consist a real health concern due to its possibility to reach drinking water and irrigation water. In this study, the active chemicals in Picovit, Clara, Drill, Endocer Givescon, Hydral, Laxofin, Maxlase, Motilium, Orapen, Scopinal, Maltvitamin, and Xilone drugs have been used as chelating agents for heavy metals remediation, they are common medicines that are widely used after their expiration. The expired drugs were used to precipitate heavy metals present in the water found in the soil around petroleum production sites. Gravimetrically, different precipitation efficiencies have been recorded due to coagulation and/or chelating with the targeted heavy metals i.e., chromium, iron, nickel, cobalt, copper, zinc, silver, cadmium, mercury, and lead. Factors of pH, Concentration of heavy metals, and the ratio of coagulant to targeted wastewater have been studied regarding the precipitation efficiency using the expired drugs (as coagulants). Results revealed that the optimum precipitation efficiencies have been recorded at applied pH, and the weight of metals precipitates were recorded. The obtained results can be considered as a preliminary study towards subsequent advanced investigations in the treatment of heavy metals from different pollution sites.

معالجة المعادن الثقيلة الموجودة في المياه المصاحبة للنفط والتربة باستخدام بعض الأدوية منتهية الصلاحية في منطقة الواحات/ ليبيا

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الكلمات المفتاحية:
معادن ثقيلة
أدوية منتهية الصلاحية
مياه مصاحبة للنفط
التربة
معالجة المياه

الملخص

المعادن الثقيلة المرتبطة بمواقع إنتاج النفط هي مصدر التلوث الرئيسي للبيئات المحيطة والمياه الجوفية. يشكل تلوث المياه الجوفية بهذه المعادن الثقيلة مصدر قلق حقيقي على الصحة بسبب إمكانية وصولها إلى مياه الشرب ومياه الري. في هذه الدراسة، تم استخدام المواد الكيميائية النشطة في عقاقير Picovit وClara وDrill و Endocer Givescon و Hydral و Laxofin و Maxlase و Motilium و Orapen و Scopinal و Maltvitamin و Xilone كعوامل مخلبية لعلاج المعادن الثقيلة، وهي أدوية شائعة تستخدم على نطاق واسع بعد انتهاء صلاحيتها. تم استخدام الأدوية منتهية الصلاحية لترسيب المعادن الثقيلة الموجودة في الماء الموجود في التربة حول مواقع إنتاج البترول. تم تسجيل كفاءات مختلفة في الترسيب بسبب التخثر و / أو الاستخلاب مع المعادن الثقيلة المستهدفة مثل الكروم والحديد والنيكل والكوبالت والنحاس والزنك والفضة والكادميوم والزئبق والرصاص. تمت دراسة عوامل الأس الهيدروجيني وتركيز المعادن الثقيلة ونسبة المخثر إلى مياه الصرف المستهدفة فيما يتعلق بكفاءة الترسيب باستخدام الأدوية منتهية الصلاحية (كمخثرات). أوضحت النتائج أنه تم تسجيل كفاءات الترسيب المثلى عند الأس الهيدروجيني المطبق، كما تم تسجيل وزن

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Article History : Received 27 Au 2022 - Received in revised form 17 November 2022 - Accepted 30 November 2021

الرواسب. يمكن اعتبار النتائج التي تم الحصول عليها بمثابة دراسة أولية نحو التحقيقات المتقدمة اللاحقة في معالجة المعادن الثقيلة من مواقع التلوث المختلفة.

1. Introduction

it is well known that medicines contain active substances in different concentrations. These active substances are able to react with heavy metals to form precipitates as in magnesium hydroxide in Laxofen. Some active substances form a complex such as penicillin and its derivatives in Orabin [1], α-d-(−) amino benzylpenicillin able to form mixed-ligand complexes with M^{2+} ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} [2]. Moxifloxacin histidine as mixed ligands (MHL) is able to form metal complexes with Mg^{2+}, Ca^{2+}, Fe^{3+}, and Zn^{2+} [3]. Carbimazole (CMZ) drugs can form metal complexes with Cu^{2+}, Ni^{2+}, and Zn^{2+} [4]. Ofloxacin drug (OFL) is able to form palladium (II) complex [5]. Theophylline (TPL) can form complexes with Mg^{2+} and Ca^{2+} ions [6]. Tenoxicam (Ten) can form complexes with Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Y^{3+} ions [7]. Non-steroidal anti-inflammatory drugs (NSAID) are able to form complexes with Fe^{2+}, Fe^{3+}, and Cu^{2+} ions [8]. Doxorubicin drug can react with Ni^{2+}, $Co^{2+,}$ and Fe^{3+} to form Metal complexes precipitates [9]. Fluoroquinolones (FQs) can be formed stable complexes with Mg^{2+} and Ca^{2+} ions [10]. The antibiotic and non-antibiotic drugs of tetracyclines were used as metal chelators [11]. Complex formation reactions of lornoxicam (LOR) drug were studied with different metal ions Cr^{3+}, Mn^{2+}, Fe $^{3+}$and Ni^{2+} chlorides and Fe^{3+}, Co^{2+}, Cu^{2+} and Zn^{2+} borates [12]. Nicotinic acid hydrazide is able to form complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} ions [13]. Pyridoxine mono hydrochloride (vitamin B_6) can form metal complexes with La^{3+}, Ce^{3+}, Sm^{3+} and Y^{3+} ions [14]. Vitamin B_3/niacin (NA) can be form complexes with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pd, Cd^{2+}, Pt and Au ions [15], Orotic acid is able to form complexes with Ca^{2+}, Mg^{2+}, Ba^{2+} and Sr^{2+} ions [16]. Thiamine hydrochloride (Vitamin B_1) react with zinc acetate in water to formed Zn (thiamine) complex [17]. Pyridoxamine, glycylglycine and imidazole are able to form complexes with Co^{2+}, Ni^{2+}, Zn^{2+} and Cd^{2+} ions [18]. Domperidone can form complexes of metals by using various derivatives of cyclodextrins [19]. pyrazinamide (PZA), nicotinamide (NAM), nicotinic acid (NIC), theophylline (TEO), captopril (CPL), tolbutamide (TBA), clonidine (CLN), guanfacine (GUAF), are able to form complexes with transition metal ions [20]. In this work the amount of precipitate of expired drugs such as Becovit, contain Calcium Pantothenate, Dexpanthenol, contain Nicotinamide, Vitamin B_6, Vitamin B_1, and Vitamin B_2. Clara, Drill, Endocare, and Gaviscon, contain (Sodium Alginate and Potassium Bicarbonate) ($KHCO_3$), Laxofin, contain Magnesium Hydroxide, Maxilase, contain Alpha-amylase (α-amylase), Motilium, contain Domperidone, Orapen, contain Phenoxy methyl penicillin, also known as penicillin V (PcV) and penicillin VK, Scopinal, contain Hyoscine butyl bromide, also known as scopolamine butyl bromide, and Xilone, contain Prednisolone which reacts with ten of heavy metal ions Cr^{3+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+}, Ag^{+}, Cd^{2+}, Hg^{2+}, and Pb^{2+} to formed coagulants or complexes precipitate to the treatment of water accompanied with oil and soil from Elkhalij company at El-Wahat / Libya.

2- Experimental

2.1. Chemical and Used equipment

100 Beakers of 250 mL Capacity; Filter Papers; Funnels; Cylinder Tester; Cup; Conical Flasks; Sensitive Balance; Standard 250 mL Beakers and measuring flasks.

2.2. Preparation of solutions

250 mL of a solution of 0.1 molar are prepared from the following materials: Cu $(NO_3)_2$, (4.6 g); Co $(NO_3)_2$-$4H_2O$, (6.2g); $AgNO_3$, (4.24g); $NiCl_2$-$6H_2O$, (5.9g); $Fe(NO_3)_3$, (10.1g); $Cr(NO_3)_3$-$9H_2O$, (10.006g); $Cd(NO_3)_2$-$4H_2O$, (7.7g); $Pb(NO_3)_2$,(7.4g); $Zn(NO_3)_2$-$4H_2O$, (6.086g); and $HgCrO_4$ (7.9602g). All solutions are prepared by the analytical method in a 250 mL measuring flask, and all chemicals are produced by Sigma company.

2. 3. Expired drugs

Used drugs and their numbers are illustrated in Table 1

Table 1. expired drugs used in this study

Drug NO.	Drug Name	Active Substance
1	Becovit	Known as Calcium Pantothenate, Dexpanthenol, Nicotinamide, Vitamin B_6, Vitamin B_1, Vitamin B_2
2	Clare	Loratadine or Ethyl 4-(8-chloro-5,6-dihydro-11H-benzo [5,6] cyclohepta[1,2-b] pyridin-11-ylidene)-1-piperidinecarboxylate
3	Drill	Dextromethorphan
4	Endocare	Ambroxol Hydrochloride
5	Gaviscon	Known as Sodium Alginate and Potassium Bicarbonate ($KHCO_3$)
6	Hederal	Butamitrate
7	Laxofin	Known as Magnesium Hydroxide
8	Maxilase	Known as α-amylase
9	Motilium	Known as Domperidone
10	Orapen	Known as Phenoxymethylpenicillin also known as penicillin V and penicillin VK
11	Scopinal	Known as Hyoscine butyl bromide or scopolamine butyl bromide
12	Multivit	B_1, B_6, B_{12}, C, and D vitamins
13	Xilone	Known as Prednisolone

2.4. Weight measurements

2 mL of the drug was added to 10 mL of heavy metal ion solution and left overnight and after precipitation, filtration and drying, all weights of all metal complexes were determined as shown in **Table 2**.

Table 2. The weight of metal-drug complexes (g) resulted from the reaction of expired drugs and heavy metal ions.

Drug	Fe	Ni	Co	Cu	Zn	Ag	Cd	Hg
1	0.95	0.617	0.953	0.878	0.5	0.367	0.248	0.56
2	0.4	0.181	0.7	0.368	1.284	0.715	0.782	2.2
3	0.35	0.221	0.342	0.017	0.307	0.29	0.71	0.55
4	0.26	0.35	0.02	0.23	0.53	1.08	0.33	0.47
5	0.4	0.05	0.25	0.23	0.19	0.17	0.16	0.23
6	0.15	0.23	0.16	0.28	0.29	0.21	0.41	0.15
7	2.22	0.23	0.58	2.61	0.45	0.52	0.8	0.64
8	0.11	0.765	0.159	0.881	0.762	0.673	0.735	0.95
9	0.63	0.11	0.22	0.60	1.24	0.62	1.32	0.72
10	0.13	0.02	0.17	0.56	0.53	0.46	0.44	1.45
11	0.41	1.07	0.24	0.16	1.19	0.67	1.02	2.21
12	0.83	0.14	0.80	0.82	0.24	0.60	0.2	0.65
13	0.02	0.17	0.09	0.19	0.10	0.06	0.21	0.25

Table3. Samples from water accompanied with oil as wastewater and soil in Elkhalij company (Elnafora) / El-Wahat

Drugs	wastewater	Soil	Cr	Pb
1-Becovit	2.94	0.33	0.481	0.66
2-Clare	1.44	0.47	0.631	0.98
3-Drill	2.84	0.5	0.609	0.61
4-Endocare	4.37	0.04	1.00	0.27
5-Gaviscon	9.95	0.05	1.51	0.34
6-Hederal	3.44	0.12	0.49	0.15
7-Laxofin	5.12	0.65	2.8	1.21
8-Maxilase	3.36	0.12	0.78	0.49
9-Motilium	5.9	0.28	1.26	1.16
10-Orapen	3.04	0.14	0.77	0.7
11-Scopinal	2.82	0.45	0.78	1.5
12-Multivitamin	1.57	0.12	0,24	1.5
13-Xilone	1.34	0.11	0.19	0.1

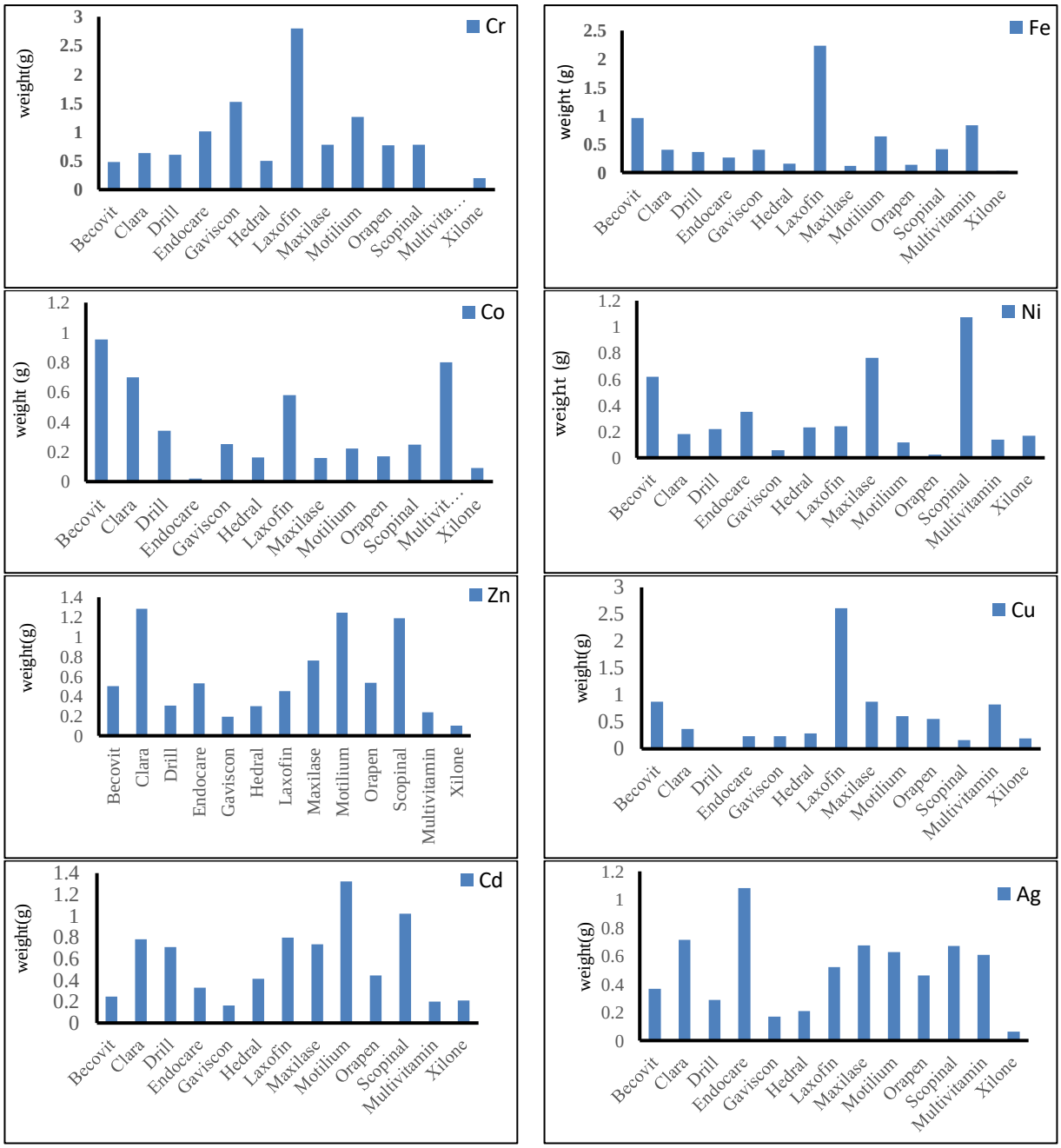
2.5. Application for water accompanied with oil and soil

For the water accompanied with oil as wastewater: 10 mL of the drug was added to 50 mL of the water sample, and after precipitation, filtration and drying, the weight of all metal complexes was determined. For the soil sample: 100 g of soil sample dissolved in 1L distilled water overnight filtrated, then 10 mL of the drug was added to 50 mL of filtrates and left overnight, after precipitation, filtration and drying, the weight of all metal complexes was determined.

3. Results and Discussion

Many complexes of expired drugs have been formed by heavy metals, and this generally leads to a change in the properties of the original compound. The structure of expired drugs allows them to form metal complexes, and expired drugs often bind with divalent ions in a ratio of 1:1 or 1:2 (metal: ligand) and with trivalent ions, in a ratio of 1:1 or 1:3, rarely 1:2. Regardless of the metal ion and ligand concentration, complex molar ratio preferences may depend on the pH.

Figure 1 explain that Laxofin forms a big precipitate with Cr ions more than other expired drugs, that the Laxofin drug contains Mg $(OH)_2$ and possibly precipitated as Cr $(OH)_2$. Moreover, Laxofin forms a big precipitate with Fe ions than other expired drugs due to precipitation as Fe $(OH)_3$ [1]. Scopinal, Maxilase, and Becovit are able to form a big precipitate with Ni ions than other expired drugs due to its containing hyoscine butyl bromide and, vitamin B, which precipitated as Ni complexes. it is observed that, when the pH of an acidic solution of pyridoxol hydrochloride and nickel (II) was increased to pH 3.0, a greenish-blue color appeared, then the color intensity was increased as the pH rose to 6.0, in which a gelatinous precipitate was formed [2-7]. Becovit, Clara, multivitamins and Laxofin are able to form a big precipitate with Co than other expired drugs due to their containing vitamin B. The reaction of zinc acetate with thiamine hydrochloride (Vitamin B1) in water produced a Zn complex of $Zn(thiamine)Cl_3 \cdot 0.4H_2O$. The resulting structure has been determined by X-ray diffraction. It was crystallizing with eight molecules in space group C_2/c of the monoclinic system. The cell has dimensions at 20 °C of a = 25.747(8), b = 8.453(3), c = 17.402(4) Å, β = 105.8(1) °, V = 3644.3 $Å^3$, D_{calc} = 1.602 g cm^{-3}. The structure has been refined by least-squares methods to a final value of 0.037 [17]. Clara, Maxilase, Motilium and Scopinal are able to form a big precipitate with Zn than other expired drugs due to its containing Loratadine, α-amylase, Domperidone and, scopolamine butylbromide, which precipitated as Zn complexes [8-15]. Clara, Endocare Maxilase, Motilium Scopinal and Multivitamin are forming a big precipitate with Ag than other expired drugs due to its containing Loratadine, α-amylase, Domperidone scopolamine butyl bromide and, vitamins B which precipitated as Ag complexes [6-20].



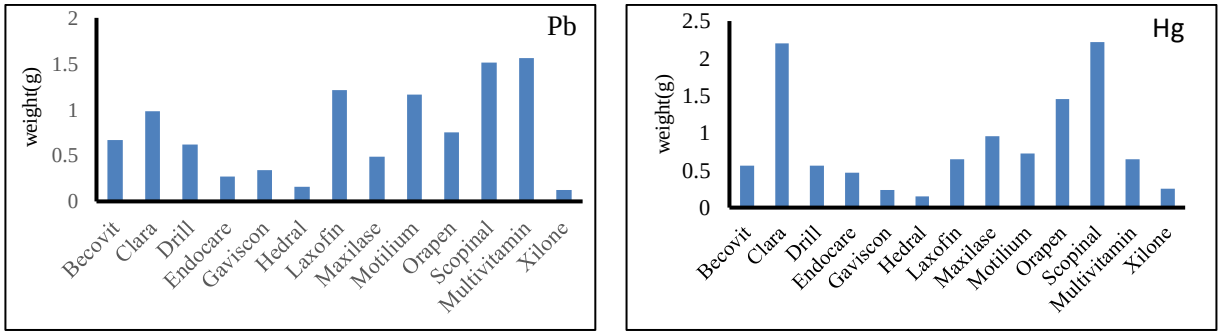


Figure 1. the precipitate weight(g) of Cr, Fe, Ni, Co, Cu, Zn, Ag, Cd, Hg and Pb complexes which may be formed by adding 2 mL of the expired drug to 10 mL of 0.1M of metal salts.

Clara, Drill, Laxofin, Maxilase, Motilium, and Scopinal can form big precipitation with Cd ions than other expired drugs due to its containing Loratadine, Acetaminophen, Magnesium Hydroxide, α-amylase, Domperidone, and, Scopolamine butylbromide, which precipitated as Cd ions complexes [5-20]. Clara, Maxilase, Motilium, Orappen and Scopinal are able to form big precipitation with Cd than other expired drugs due to its containing Loratadine, α-amylase, Domperidone, Penicillin V, Scopolamine butylbromide which precipitated as Cd complexes [6-10]. Clara, Laxofin, Motilium, Orappen Scopinal, and Multivitamin are able to form big precipitation with Pb ions than other expired drugs due to its containing Loratadine, Magnesium Hydroxide, Domperidone, Penicillin V, Scopolamine butylbromide, and, Vitamins B, which precipitated as Pb complexes [12-20].

Ampicillin can exist as a zwitterionic species. Protonated ampicillin $AmpH_2^+$ contains –COOH and the $–NH_3^+$ groups which are successively deprotonated in the pH range 2–4 and 6–8, respectively. Above pH 12, amp- tends to give a drawn-out buffer region, obviously due to partial deprotonation of the amide (-CONH-) moiety. At physiological pH, ampicillin remains in a fully deprotonated amp- form, which coordinates metal ions as an (N, O) bidentate ligand in the pH range 5 < pH < 8 using the amino nitrogen and the amide carbonyl oxygen atoms. The thiazolidine S atom is unlikely to coordinate this mode, obviously due to angle strain. The amide nitrogen can bind metal ions only on deprotonation. The (N, O) coordinated amp- undergoes amide deprotonation at pH > 8, and the resulting H~ amp2- ion coordinates as an (N, N, S) tridentate ligand using the amino nitrogen, deprotonated amide nitrogen, and the thiazolidine S atoms [4].

Table 2 explains the following trends:

- The highest reacted heavy metal ions were Fe, Co, Cu, and Pb ions, which form the highest precipitates with Becovit expired drug.
- The highest reacted heavy metal ions with Clara expired drug were Zn and Hg.
- The highest reacted heavy metal ions with Drill expired drug were Cr, Co, Zn, Ag, Cd, and Pb ions, which form the highest precipitates.
- The highest reacted heavy metal ions with Endocare expired drug were Cr, Ni, Zn, Ag, and Hg ions.
- The highest reacted heavy metal ions with Gaviscon expired drug were Cr and Pb ions.
- Hedral expired drug form the highest heavy metal complex precipitates with Cr, Ni, Cu, Zn, and Cd ions [15].
- The highest heavy metal ions that reacted with Laxofin expired drug were Cr, Cu, Cd, and Pb.
- Maxilase expired drug form the highest heavy metal ions precipitate with Cr, Ni, Cu, Ag, Cd and Hg ions.
- The highest reacted heavy metal ions with Motilium expired drug were Cr, Zn, Cd, and Pb ions.
- The highest reacted heavy metal ions with Orapen expired drug were Cr, Cu, and Hg
- Scopinal expired drug form the highest heavy metal complexes with Ni, Zn, Cd, Hg, and, Pb ions.
- the highest-reacted heavy metal ions with Multivitamin expired drug were Fe, Co, Cu, Ag, Hg and Pb.
- The Xilone expired drug formed the highest heavy metal complexes precipitate with Cr, Ni, Cu, Cd, and Hg ions.

Some of the formation constants of the binary complexes of Ni (II), Co (II), Zn(I1) and Cd(I1) metal ions with Glygly were previously studied and suggested to form a stable hex- a coordinated species. Similarly, Zn (II) and Cd(II) form regular 1:1 and 2:1 species where Glygly was bidentate. These complexes were less stable than the corresponding glycine metal complexes. However, the inability of Zn (II) and Cd(I1) to deprotonate the peptidic proton may be due to the precipitation at a pH of 8.5 [18].

Table 3 explains that Becovit, Clara, Drill, Endocare, Gaviscon, Hedral, Laxofin, Maxilase, Motilium, Orapen, Scopinal, Multivitamin and Xilone are given large precipitations than other expired drugs due to their containing Sodium Alginate but others containing Vitamins B, Loratadine, Acetaminophen, sodium Alginate, Saponins, Magnesium Hydroxide, α-amylase, Domperidone, Penicillin V, Scopolamine butylbromide, Vitamins B and, Prednisolone.

Figure 2 shows the comparison between the lowest molecular weight of the heavy metal used (Cr) and the highest molecular weight of the heavy metal used (Pb) with the same heavy metals found in oily water and soil that precipitate due to expired drugs. It was found that the water associated with oil contains a proportion of Very high heavy metals that is higher than standard solution Cr ion 520 ppm, Pb ion 2070 ppm, but soil with low heavy metal content is lower than standard solution Cr ion 520 ppm, and lead ion 2070 ppm.

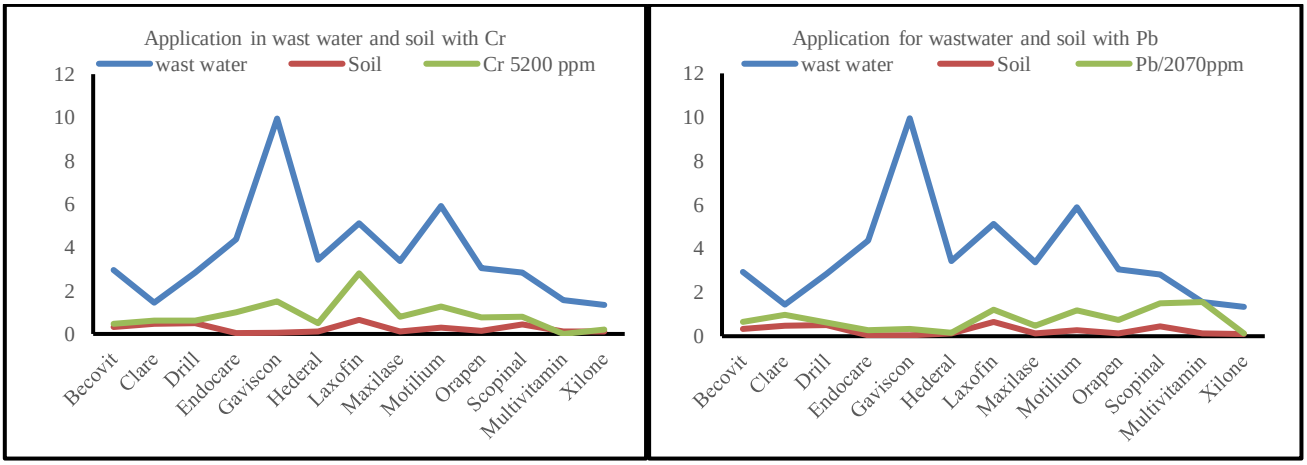


Figure 2. The weight (g) of heavy metals precipitate with expired drugs from water accompanied oil and soil compared with 520 ppm Cr and 2070 ppm Pb concentrations

4. Conclusions

Expired drugs have the ability to interact with heavy metal ions and form precipitate complexes with different efficiencies because expired drugs had a chelating compound that can form complexes with heavy metal ions, and precipitate them, Picovit: Fe, Ni, Co, Clara: Zn, Co, Ag, Hg, Drill: Cr, Cd, Endocer: Ag, Givescon: Cr, Hydral: Cd, Laxofin: Cr, Fe, Cu, Co, Maxlase: Ni, Motilium: Zn, Cd, Oraben: Hg, Ag, scopinal: Ni, Zn, Cd, Hg, Maltvitamin: Co, Pb and Xiylone: Ni, Cd, Hg. Then used to treat water accompanied with oil, and reduce the absorption of soil, and plants because of their great damage to human health.

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