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5. SUMMARY

This study was conducted to:(i) survey As and Cd contents in soils and waters, (ii) study the adsorption isotherms of arsenic and cadmium by two soils (varied in their texture and calcium carbonate content),zerovalent iron (ZVI), and synthetic mineral (goethite), (iii) investigate the effect of pH on adsorption and desorption of As and Cd from some adsorbent materials, (iv) assess the competitive adsorption of (As, Se),(As, S),(As, P),(As, Mo) and (Cd, Co) on the tested materials and (v) study the adsorption Kinetics of As on the goethite and zerovalent iron (ZVI).

A SURVEY STUDY ON AS AND CD IN SOILS AND WATERS:

This experiment was carried out to evaluate the pollution of soils and waters in different locations (Kaliubiya, Giza, Cairo and New vaelley Governorates).

Samples of soils and waters were collected and analyzed to determine arsenic and cadmium as affected by the industrial activities and irrigation with different wastewaters in the studied areas.

Laboratory Studies:

Experiment I:(Adsorption isotherms)

This experiment was carried out to evaluate adsorption of arsenic and cadmium by tow soil samples (loamy and clay loam soil with 4.83 and 27.10 %$CaCO_3$, respectively), pure zerovalent iron and synthetic minerals (goethite) with back -ground of sodium chloride.

A portion of one gram of each soil sample and 2.5 mL from goethite and 0.01 gram of zerovalent iron (ZVI) were equilibrated for an hour in a 50-mL reaction vessel with a solution of ($Na_2HAsO_4.7H_2O$) and cadmium nitrate having 0-50 µg (As or Cd) mL^{-1}, in presence of 0.1 M NaCl as a back ground

Experiment II:(pH envelopes):

Effect of pH on As (V) and Cd adsorption on soils was tested through an experiment similar to that of As (V) and Cd adsorption isotherms except the pH values of soil and As or Cd suspension were adjusted to be in the range of 3.0 to 12.0 and the concentration of As or Cd was 10 µg mL^{-1}.

To study the effect of pH on Arsenic or cadmium adsorption on goethite and zerovalent iron; an experiment was conducted as follows: to a 50-mL reaction vessel 2.5 mL goethite suspension or 0.01 g zerovalent iron, 2.5 mL of electrolyte back ground (1.0 M NaCl) and 250 µL of arsenic in the form of As(V) or cadmium (stock solution 1000µg mL^{-1}) were added and the volume was completed to be 25 mL with deionized water. The concentration of As or Cd in the reaction vessels was 10µg mL^{-1}.The pH in the reaction vessels was adjusted to be between 3 to 12..

Experiment III:(Competive adsorption):

To study the competition between (As and Se, As and P, As andMo As and SO4) and (Cd andCo) on the surfaces of synthetic minerals and zerovalent iron 2.5 mL and 0.01gram from goethite, and zerovalent iron, respectively were shaken , after adjusting the pH was adjusted to be in the range of 3.0 to 12.0 , with 25 mL of distilled water containing four different ratios (1:0,1:1,1:2 and 2:1) of As or Cd to the previous mentioned oxyanions in case of As and Co in case of Cd.

Experiment IV:(Kinetics of As adsorption)

This experiment was conducted on goethite and zerovalent-iron as adsorption kinetics of As(V) were evaluated on both adsorbents at pH 5 and 9, and initial As concentration of 10 μg mL^{-1} which equals 0.126 μmol mL^{-1}. A portion of 50 mL goethite suspension or 1 g zerovalent iron was placed in a 500 mL polyethylene patch reactor, 50 mL of 1 M NaCl were added to the reactor and the volume was brought to volume (500 mL) using deionizeed water.

Experiment V:(Desorption of As and Cd)

A portion of one gram of each soil (Loamy or Clay loam) was equilibrated with 25 mL of As (V) or Cd solution having 10-100 μg As or Cd mL^{-1} in presence of 0.1 M NaCl (ionic strength buffer) for 24 h. Samples were shaken for 16 h, centrifuged, filtered and the filtrates were collected. To the settled samples which remained in the centrifuge tubes 20 mL of 0.005 M DTPA solution were added. The tubes were shaken for 2 h, centrifuged at 3000 rpm for 30 min, filtered and As or Cd concentration in the filtrate was determined.

Goethite and Zerovalent iron:

A portion of 50-mL goethite suspension or 1g zerovalent iron was equilibrated with solution having 10 µg As (V) mL^{-1} after adjusting the pH to be 5 or 9 Subsamples (10 mL) were taken, and placed in centrifuge tubes, and then 10 mL of each one of the following: phosphate , sulphate, molybdate, or selenate were added to obtain the desire ratio between As: PO_4 or SO_4 or MoO_4 or selenate (1: 100). The pH of samples was adjusted to be in the range of 3 to 12, and samples ware shaken for 4 h, centrifuged for 30 min at 3000 rpm and filtered through 0.2-µm membrane filters.

The obtained results of this study will be summarized under the following two main topics:

(1) Results of the survey study and (2) Results of the laboratory studies

Survey of the occurrence of As and Cd in the selected waters and soils:

Arsenic: *The highest concentration of As (5.54 µg L^{-1}) was found in waste water of main drain of cook factory in El-Tabeen, Helwan, while the lowest concentration of As (0.17 µg L^{-1}) was existed in well water of Gehna in New Valley province.. *The detected range of As did not exceed the water standard level suggested by the Environmental Protection Agency (EPA) of America which was amounted to be 10 µg L^{-1}**.** *The obtained values of As did not exceed to induce a toxicity hazard for both of human being and animals whose their food staff originates mainly from such soils as the permissible level of As in soil is 20 mg L^{-1}

Cadmium: *The highest Cd concentration existed in Zenein station of treating sewage waters, while the lowest value was found in water well called Habis located in New Valley area. * Only one soil sample did not show a detected concentration of Cd. Either water or soil contents of Cd did not exceed the permissible levels of them which are 0.01 mg $L^{-1}$for the former and 20 mg kg^{-1} for the later. *As and Cd in waters and soils under investigation did not consider to be harmful to the human-being except with the highest concentration of water concomitant with intensive consumption of it.

Laboratory studies :

Experment I: Adsorption isotherms of arsenic and cadmium)

Soils

Arsenic.: *Data of As (V) adsorption on both soils were fitted to the linear form of the adsorption isotherm equations of Langmuir and Freundlich . *Adsorption of arsenate obeyed the Langmuir adsorption isotherms with coefficient of determination (r^2) of 0.796 and 0.610, respectively. Also, adsorption of As (V) on both soils was highly fitted to Freundlich adsorption isotherms with coefficient of determination (r^2) of 0.863 and 0.968, respectively.

Cadmium: *Adsorption maxima of Cd on clay loam soil under different concentrations of Cd were higher than the corresponding ones observed with loamy soil. *It seems that, each one of the tested soils adsorbed appreciable quantities of Cd as the adsorption maxima of loamy and clay loam soils were 1428 and 1666 µg Cd g^{-1}**.**The results of Cd adsorption on soils were highly fitted to Langmuir and Freundlich isotherms.

Goethite

Arsenic: *arsenate was adsorbed in large quantities at pH 5 comparing to pH 9.

*The equilibrium As concentrations (C, µg As mL^{-1}) were highly fitted to the linear form of adsorption isotherm equations of Langmuir and Freundlich with coefficients of determination (r^2) of 0.992 and 0.989, at pH 5 and 9, respectively. *The adsorption maxima for arsenate on goethite were 11111 and 5000 µg As (V) g^{-1} goethite at pH 5.0 and 9.0. *The adsorption maxima for arsenite on goethite as calculated from the Langmuir isotherms are 10000 µg As (V) g^{-1} goethite at pH 5.0 and 9.0.

Cadmium.: * Adsorption of Cd on goethite at pH 5.0, was increased gradually with increasing equilibrium concentration of Cd and *At pH 9.0 the adsorbed Cd increased with increasing Cd concentration with the highest adsorption of 173 µg Cd g^{-1} goethite in case of using the highest initial Cd concentration of 60 µg Cd mL^{-1}, while at pH 5.0 similar trend was achieved with more increases of Cd adsorption at the tested initial Cd concentrations (3-60 µg Cd mL^{-1}) *Adsorption data of Cd on goethite at pH 5.0 and 9.0 obeyed Langmuir and Freundlich isotherms with (r^2) values of 0.933,0.961,0.850 and 0.919 . Adsorption maxima for Cd on goethite are 435 and 188.7 µg Cd g^{-1}goethite at pH 5.0 and pH 9.0, respectively.

Zerovalent iron

Arsenic: *Adsorbed As (V) on ZVI at pH 5.0 was increased gradually with increasing equilibrium concentration of As and the highest adsorption of 114.678 mg As g^{-1} zerovalent iron (ZVI) was recorded with the highest initial As concentration of 60 µg mL^{-1}. *Surface saturation with As (V) was not complete and maximum adsorption was not achieved. At pH 9 As (V) was adsorbed in small quantities as compared to pH 5 and the amount of adsorbed As (V) per gram (ZVI) decreased by a proportion higher than that at pH 5, the highest amount of adsorbed As was 69.315 mg g^{-1}under the condition of the experiment. *Adsorption data of As on zerovalent iron (ZVI) at pH 5 and 9 obeyed Langmuir isotherms with (r^2) values of 0.989 and 0.953. Also the obtained data obeyed Freundlich isotherms with (r^2) values of 0.768 and 0.873 at pH 5 and 9, respectively. *The adsorption of As (III) on zerovalent iron (ZVI) was increased gradually with increasing equilibrium concentration of As (III) and the highest value was obtained with increasing pH from 5 to 9. *Zerovalent iron (ZVI) showed a good ability to adsorb either As (V) or As (III) at the selected pH values (5 and 9). * The adsorbed As in both forms exceeded that occurred on goethite. This result should be taken into consideration when the purification of water from As is needed. Zerovalent iron (ZVI) is easy to be obtained and to be used in manufacturing the columns of water purifiers. Beside the advantages of zerovalent iron (ZVI), there is a disadvantage of it which is it could not last for long time and it could be decomposed.

Cadmium :*Cadmium adsorption on (ZVI) obeyed Langmuir isotherms either at pH 5 or 9 with values of determination (r^2) of 0.965 and 0.962 at pH 5 and 9, respectively.*The highest adsorbed quantities of Cd at pH 9 may be due to the adsorption and precipitation processes which played an important role in Cd chemistry in solutions.*In case of Freundlich isotherms, the obtained data showed highly significant (r^2) values at pH 5 and 9. Also, the obtained data showed the highest Cd adsorption maxima of 8.199 and 89.104 mg Cd g^{-1} (ZVI) at pH 5 and 9, respectively. *The obtained results indicate the hypothesis of ZVI could be efficient to adsorb and retain Cd in solutions of high Cd concentrations. It could be effectively used in the columns of water purifiers.

Experiment II :Adsorption envelopes (adsorption versus pH)

Soil

Arsenic:*Under the condition of this experiment the highest As adsorption by soil was 59.5 µg As g^{-1}soil at pH 5.0. Adsorbed As was gradually decreased with increasing pH > 5.0 and the lowest value occurred at pH 12, when 6.4% of total As was adsorbed by soil.

Cadmium:*Aadsorption of Cd showed an opposite behavior to arsenate as its quantities increased with increasing pH. The highest Cd adsorption was noticed at pH 7.0 with a constant adsorption values with pH >7.0.The highest Cd adsorption was 98 µg Cd g^{-1} soil which corresponded to 40% of total added Cd

Goethite

Arsenic: *The adsorption envelopes for arsenate at the initial solution concentration equivalent to 10 µg As mL^{-1} indicated adsorption of nearly 100% of total arsenate added throughout the pH of 3-4. With increasing pH> 4, arsenate adsorption declined sharply to be 30% of the total As added at pH 12. *Arsenate adsorption decreased almost linearly from almost 3119 µg As g^{-1}

goethite, at pH 4 to 938 µg As g^{-1} goethite at pH 11. The lower adsorption of arsenate at high pH values is attributable to an increased repulsion between the more negatively arsenate species and negatively charged surface sites

Cadmium:* Adsorption of Cd showed an opposite behavior to arsenate as its adsorbed quantities increased with increasing pH. The highest Cd adsorption was noticed at pH 7.0 with a constant adsorption values with pH >7.0.The highest Cd adsorption was 3099 µg Cd g^{-1} goethite which corresponded to 49% of total added Cd.

Zerovalent iron (ZVI) :

Arsenic:*The adsorption envelopes for arsenate at the initial solution concentration equivalent to 10 µg As mL^{-1} indicated adsorption of nearly 100% of total arsenate added throughout the pH of 3-4. With increasing pH > 4, arsenate adsorption declined sharply to be 16% of the maximum adsorption of As at pH 12 and at lower pH values, arsenate was retained in larger amounts *The adsorption envelopes exhibited broad adsorption maxima for arsenate in the pH range of 3-4 which was followed by a gradual decline with increasing pH > 4. Such decrease coincided approximately with the second pKa (6.9) of H_3AsO_4. *Arsenate adsorption decreased almost linearly from almost 24960 µg As g^{-1} ZVI, at pH 4 to 4160 µg As g^{-1} ZVI at pH 11.

Cadmium: *The highest Cd adsorption was noticed at pH 7.0 with a constant adsorption values with pH >7.0.The highest Cd adsorption was 24973 µg Cd g^{-1} ZVI which corresponded to 99 % of total added Cd.

Experiment III :Competitive adsorption

Arsenate and phosphate: *In the absence of PO_4, adsorption of As on goethite was slightly decreased with increasing pH. At pH 7.0 a quantity of 2891 µg As g^{-1} was adsorbed from the added As(V) per gram goethite, with increasing the pH above pH 9.0 the adsorbed As was decreased to be 1662 and 945 µg As g^{-1} goethite at pH 11.0 and 11.8, respectively. *Adsorption of As (V) was decreased with increasing pH when As (V) was added alone or with PO_4 at As : P ratios of l : 0,1:1 and 1 : 2 However, more pronounced increases in As (V) adsorption was noticed when As (V) was added at 2: 1 As: P ratio with all tested pH values. *The affinity of goethite to As (V) was affected largely by pH and by As (V) concentration in equilibrium solution. The lowest As (V) adsorption was noticed with As (V) : P ratio of 1 : 2 particularity at the high pH values. *It could be mentioned that PO_4 could not compete well with arsenate on the specific sites of As if its ratio to As was less than 2:1.*These results indicate that the preference of adsorption sites to As was mainly affected by pH values and the concentration of associated oxyanions.

**Arsenate and selenate: ***With As:Se ratio of 1:2 the adsorbed As was decreased more as compared with other ratios. *Selenate has competed with As on the adsorption sites and reduced the amount of As adsorbed on goethite to be 68.7%. Such decrease in As adsorption was greater than that obtained with PO_4 under the same condition.*Increasing the initial concentration of As comparing with selenate or any other oxyanions alleviates the effect of competing oxyanions as indicated with As:Se ratio of 2:1.

Arsenate and molybdate: *More than 95% of As was adsorbed below pH 4.0 in single Mo anion and binary MoO_4 anion systems on goethite. These data suggest that MoO_4 occupies a fraction of the pH-dependent of As (V) adsorption sites on goethite and there is another distinct fraction of sites has higher affinity for As or MoO_4 at low pH.

Arsenate and sulfate: *The preference of the adsorbent to As (V) over S was indicated when they added together. Up to pH 10.0 sulfate failed to compete with arsenate on As (V) adsorption sites.

Cadmium: *The highest adsorption of Cd was achieved with using 2:1 Cd: Co ratios while the lowest Cd adsorption occurred with using 1:1 Cd: Co ratio .*The quantities of Cd adsorbed at pH 5.5 and with Cd: Co ratios of 1:0,1:1 and 1:2 were higher than values obtained at pH 4.0. At pH 9.3 the adsorption of Cd was independent from Cd :Co ratios as it recorded almost 100% with all tested ratios

Zerovalent iron.(ZVI)

Arsenate and phosphate: *Pronounced increases in As (V) adsorption was noticed when As was added at 2: 1 As: Se, P, Mo and S ratios. The affinity of ZVI As,Se, P and Mo was affected largely by pH and by As concentration in the equilibrium solution. * The preference of the adsorbent to As over P was indicated when they added together as As (V) adsorbed amount was increased gradually with increasing pH with slight differences as compared with no P addition. However, phosphate was more affected by As and the amount of adsorbed arsenate recorded 23590 µg As g^{-1} at pH 4.0, decreased to 15620 µg As g^{-1} at pH 9.5 and decreased sharply with increasing pH to achieve

983 µg As g^{-1} at pH 12.0 *Adsorption of As was decreased with increasing pH in presence and absence of P. At the 10 µg mL^{-1} initial concentration, As (V) surface coverage reached maximum of 24960 µg Asg^{-1} on ZVI at pH 3.0. *At 10 µg As mL^{-1} As (V) starting concentration As (V) was 100% adsorbed on (ZVI) below pH 7, Both As (V) and P single amnions displayed broad adsorption envelopes with 100% adsorption of As (V) below pH 6 and 98% when added P ratio (1:l) and decreased of As adsorption when added 2:1As: P ratio.

Arsenate and selenate:*The adsorption of As (V) was decreased with increasing pH. When As (V) was added alone or with Se (IV) at Low As : Se ratio (l : 0, l : l and 1:2). more difference in Se (IV) adsorption when added in the ratio of l : 2. *Selenate appreciably competed with As on the adsorption sites and reduced the amount of As adsorbed on ZVI. Such decrease in As adsorption was greater than that obtained with PO_4 under the same condition.

Arsenate and molybdate:*More than 95% of As was adsorbed below pH 4.0 in single Mo anion and binary As (V) Mo anion systems on (ZVI).

Arsenate and sulfate: *The preference of the adsorbent to As (V) over SO_4 was indicated when they added together as As (V) adsorbed was decreased with increasing pH with slight deference as compared with no SO_4 addition. However, SO_4 was mot affected by As.

Cadmium:*The highest adsorption of Cd was achieved with using 2:1 Cd: Co ratios while the lowest Cd adsorption occurred with using 1:1 Cd:Co .The pH envelopes study reveal that the quantities of adsorbed Cd were different and depended on Cd :Co ratio.

Experment IV: Kinetics of arsenic adsorption.

.goethite.: * Arsenate adsorption at pH 5.0 increased very fast in the first 2 min. of the reaction and a portion of 99% of the added As was adsorbed. *Then, adsorption reaction proceeded gradually to reach 99.9.% of the added As after 1.0 h of the reaction initiation.

*At pH9, arsenate adsorption was considerably faster with increasing time from 0.0 to 40 min. with low initial As concentration. The faster As(V) adsorption may be due to the formation of monodentate complex with Fe $^{3+}$ atoms of goethite surface.

Zerovalent iron. (ZVI): * Arsenate adsorption at pH 5.0 increased very fast in the first 4.0 min of the reaction and a portion of 100% of the added As was adsorbed. *At pH 9, arsenate adsorption was considerably faster with increasing time from 0.0 to 40 min with low initial As concentration. However, at pH 5 adsorption of arsenate was faster than adsorption of arsenate. at pH 9.0

Experiment V :Desorption of arsenic and cadmium.

Soil

Arsenic:*.Desorped As µg g^{-1} from loamy soil increased gradually with increasing initial As (V) concentration. * A slight increase in the desorbed As was observed with increasing its initial concentration from 30 to 40,50 to 60 and from 90 to 100 µg As mL^{-1}. *The highest desorption percentages, i.e., 39.0, 39.4 and 40.5 % were accompanied with initial concentrations of 90,30 and 80 µg As mL^{-1} respectively. *Concerning clay loam soil, a high increase in desorbed As was noticed with increasing the initial As concentration from 20 to 30,70 to 80 and 90 to 100 µg As mL^{-1}. However, moderate increases with increasing the initial As concentration from 10 to 90 µg As mL^{-1} *Desorbed As(V) decreased gradually with increasing As coverage on surfaces of clay loam.

Cadmium:*Desorpion of Cd increased with increasing its initial concentration the highest desorption increases were attained with increasing initial Cd concentration from.10 to 20 µg Cd mL^{-1}.*Concerning clay loam soil, a sharp increase in desorped Cd was noticed with increasing the initial Cd concentration from 10 to 40 µg Cd mL^{-1} followed by gradual increases with increasing initial Cd concentration from 10 to 80 µg Cd mL^{-1}

Effect of phosphates on arsenic desorption from goethite:

* Phosphate had the greatest effect on As (V) desorption from goethite at pH 3.0 (31.6%) and As desorption was slightly increased with increasing the pH up to 7.0 (33%). Above pH 7.0, the desorption of As (V) increased to approximately (70.6%) at pH 12. In presence of phosphate in a concentration 100 times as arsenate, and at pH (9) phosphate had the greatest effect on As (V) desorption at pH 3 (43.7 %) and As desorption increased with increasing the pH up to 7.0 (46%). Above pH 7, the desorption of As (V) increased to a approximately 75.5 % at pH 12.

Effect of sulphate on Arsenate desorption on goethite:

*Sulfate has no appreciable effect on As(V) desorption at pH 3.0 (0.34%) and As desorption was negligible with increasing the pH up to 7.0 (0.34).Above pH 7, the desorption of As (V) increased to approximately (59.8%) at pH 12.0.

Effect of molybdate on arsenate desorption on goethite: *Molybdate has the greatest effect on As (V) desorption at pH3.0 (32%) and As desorption was decreased with increasing the pH up to pH 7.0 (0.10%) Above pH 7.0, the desorption of As (V) increased to approximately (58.9%) at pH 12.0 in presence of molybdate at initial concentration ratio of 100:1 (MoO_4:As).

Effect of phosphate on arsenic desorption from zerovalent iron: *phosphate had the greatest effect on As (V) desorption at pH3.0 (10.1%) in case of pH 5.0 and As desorption decreased with increasing the pH up to pH7.0 (7.08%). Above pH 7.0, the desorption of As (V) increased to approximately (48.1%) at pH 12.0 in presence of phosphate and initial adsorption pH of 5.0, while at the initial adsorption pH of 9.0 phosphate had the greatest effect on As (V) desorption at pH3.0 (23.5%) and As desorption decreased with increasing the pH up to 7 (22.09%). Above pH 7.0, the desorption of As(V) increased to approximately 55.7% at pH 12.0 in presence of phosphate and arsenate at a concentration ratio of (100:1).

Effect of sulphate on arsenic desorption from zerovalent iron:*Sulfate had no effect on As (V) desorption at pH3.0 as a very less As quantities were desorbed (0.28%) and As desorption did not change with increasing the pH up to 9.0 (0.08%). Above pH 9.0, the desorption of As (V) increase to approximately (45.5%) at pH 12.0 in presence of sulphate and at initial pH of 5.0. While at pH 9.0 sulphate showed the lowest effect on As (V) desorption at pH 3.0 (0.93%) and As desorption decreased with increasing pH up to pH 8.0 (1.79%). Above pH 8.0, the desorption of As(V) increased to approximately (65.8%) at pH

12.0 in presence of sulphate to arsenate at concentration ratio of (100:1).

Effect of molybdate on arsenic desorption from zerovalent iron: * As desorption decreased sharply with increasing the pH up to 7.0 (0.00). Above pH 7.0, the desorption of As(V) increased to approximately (39.9%) at pH 12.0 in presence of molybdate and initial adsorption pH of 5.0. At pH 9.0 molybdate showed the greatest effect on As(V) desorption at pH 3.0 (51.93%) and As desorption decreased with increasing the pH up to pH 7.0 (1.30%). Above pH7.0, the desorption of As(v) increased to approximately (55.8%) at pH 12.0. in presence of molybdate at a concentration of (100:1, MoO_4:As).

الملخص العربى

تهدف هذه الدراسة الى : *حصر الأراضى والمياه الملوثة بعنصرى الزرنيخ والكادميوم .*دراسة ثوابت الأدمصاص لعنصرى الزرنيخ والكادميوم على نوعين من الأراضى يختلفا فيما بينهما فى محتواهما من الطين وكربونات الكالسييوم وكذلك على برادة الحديد النقية عديمة الشحنة واكسيد الحديد المحضرمعمليا وكذلك دراسة تاثير رقم ال pH فى محلول الاتزان على ادمصاص و عكس الادمصاص الخاص بالزرنيخ والكادميوم بواسطة الأرض و برادة الحديد النقية عديمة الشحنة واكسيد الحديد المحضر معمليا وكذلك دراسة حركية الادمصاص لعنصر الزرنيخ وكذلك الادمصاص التنافسى بين الزرنيخ والسلنيوم وكل من الفوسفات والكبريتات والمولبيدات وكذلك بين الكادميوم والكوبلت .

ولتحقيق أهداف هذه الدراسة تم اجراء الأتى:

1)الدراسة الحصرية

تم أخذ عينات

تربة ومياه من بعض الأماكن(القليوبية-الجيزة-القاهرة -الوادى الجديد) الملوثة بالتلوث