

Reuse of Wastewater in Arid and Semiarid Regions for Agricultural and Industrial Uses by Adsorption on Chemically Activated Sewage Sludge as Low Cost Adsorbent

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Abstract: Sewage sludge carbon is prepared by chemical activation of sewage sludge, the new adsorbent was used for removal of the heavy metals Cd, Pb, Cu and Mn from wastewater. The chemical activators used were 5M ZnCl₂, 3M H₂SO₄, 3M H₃PO₄, 5M ZnCl₂: 3M H₂SO₄, 5M ZnCl₂: 3M H₃PO₄. The effect of several parameters (pH, initial metal ion concentration, adsorbent dose, contact time and solution temperature) on the adsorption capacity of the studied metals was evaluated by batch experiments. The results revealed that sewage sludge activated by 5M ZnCl₂ : 3M H₃PO₄ (1:1) followed by pyrolysis at 650°C [ASS_{Z.P (1:1)}] selected as a new and effective adsorbent for the removal of Cd(II), Pb(II), Cu(II) and Mn(II). The adsorption of the metals by ASS_{Z.P (1:1)} increased with increasing pH and adsorbent dosage, while it decreased with increasing initial metal concentration. From batch adsorption data the optimum conditions for the adsorption of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_{Z.P (1:1)} adsorbent were 1 gmL⁻¹ adsorbent dosage, 1 hour contact time, 10 mgL⁻¹ initial metal concentration, 25°C solution temperature and pH 8, 5, 6 and 9 for Cd(II), Pb(II), Cu(II) and Mn(II), respectively. The data obtained from sorption isotherms of metal ions on ASS_(ZP1:1) adsorbent fit well to linear forms of Langmuir, Freundlich and Scatchard isotherm models. These findings suggest new strategies for improving metal ion removal from domestic and industrial wastewater and reuse it for agricultural uses in arid and semiarid regions.

Key words: Adsorption • Heavy metals • Activated carbon • Sewage sludge • Wastewater treatment

INTRODUCTION

Environmental pollution with organic compounds (dyes, pesticides and pharmacological) and inorganic pollutants (toxic heavy metals) increases with increasing industrial and human activities. Most of pollutants or their degradation products at sufficiently high concentrations are toxic for aquatic and terrestrial environment. The main sources of fresh water pollution can be attributed to a discharge of untreated sanitary and toxic industrial wastes, for this reason treatment of wastewater and safe disposal of solid waste is one of the most important environmental issues [1-3]. Sewage sludge can be defined as the residue generated from the treatment of sewage wastewater. The two principal types of sludge are primary sludge and secondary sludge. Primary sludge constitutes the material collected from the primary settling tanks employed in wastewater treatment plants. Secondary sludge known as biological sludge constitutes the sludge

generated from the biological treatment of the wastewater drained from the settling tanks [4]. Sewage sludge contains organic matter, nitrogen, phosphorus, potassium, calcium, sulphur and magnesium. Moreover, it may also contain pollutants such as heavy metals, organic pollutants and pathogens [5]. Also, due to the unstable nature of biomass, inadequate sewage sludge disposal may cause environmental impact and health problems [6].

The conventional disposal options for sewage sludge include landfill, application of farmland, sea dumping and land reclamation. So, soil and water affected by potential pollution by heavy metals [7]. Recently the numbers of development technologies were found for converting the sewage sludge from hazard wastes to more useful material such as: (i) The recovery of phosphorus from sewage sludge incineration ash. (ii) Composition of activated carbon from sewage sludge and used it as adsorbent for dioxin of a garbage incineration. (iii) Energy

recovery by digests the biomass as well as sewage sludge in digestive tank by ultrasonic treatment and make the digestion gas emission rate increased and uses it for generation of electricity. (v) Production of methane from mixing organism waste of garbage and sewage sludge (fermentation process) and used the collected methane for generation of electricity and produce activated carbon from the dehydration sludge [8]. Sewage sludge contains high organic content (60-80%); therefore sewage sludge can be used for the production of cost-effective activated carbons [7, 9-11].

The activation process of sewage sludge involves chemical and physical activation. Chemical activation path involves impregnation of the raw sewage sludge with chemical such as phosphoric acid [12], potassium hydroxide [13] and zinc chloride [14, 15].

Various types of activated carbons were developed from organic sewage sludge using H₂SO₄, H₃PO₄ and ZnCl₂ as chemical activation reagents [16]. Fan and Zhang [17] prepared activated carbon from sewage sludge by the paralysis at the 500°C for 3h. Phuengprasop *et al.* [18] used sewage sludge modified with iron oxide as adsorbent to remove Cu (II), Pb (II), Cd (II) and Ni (II) from aqueous solution. Rashed [19] used washed sewage sludge (WS) and sludge activated carbon (AS) as adsorbents for removal of Acid Blue 93 from industrial wastewater. Hammami *et al.* [20] studied the effect of pH and biomass concentration on the biosorption of Cu (II), Pb (II), Cd (II) and Ni (II) using activated sludge.

This study aimed to prepare new adsorbents from sewage sludge by treatment with the chemical activators, 5M ZnCl₂, 3M H₂SO₄ and 3M H₃PO₄, as well as a mixture of 5M ZnCl₂: 3M H₂SO₄ and a mixture of 5M ZnCl₂: 3M H₃PO₄ in different ratios (1:1, 1:2 and 2:1 by v: v). The adsorption of Cd, Pb, Cu and Mn onto the developed adsorbent was investigated. The effect of several parameters, such as pH, adsorbent dosage, contact time, solution temperature and initial metal concentrations was evaluated to better describe the adsorption process

MATERIALS AND METHODS

Sewage Sludge Collection: Sewage sludge sample (5kg) was obtained from disposal sewage sludge from the Kima plant (biochemical treatment) in Aswan city, Egypt. The sludge sample was air dried in a clean place and oven dried at 105°C for 24h. After cooling the sample was kept in a polyethylene container until the analysis. The chemical composition of sewage sludge was listed in

Table 1: Chemical composition (%) of raw sewage sludge.

C	O	Mg	Al	Si	P	S	Ca	Fe
64.05	6.3	0.63	2.4	8.36	1.62	2.44	9.81	4.40

Wastewater Samples Collection: 500 ml wastewater sample was collected from a wastewater drain in the laboratory for heavy metals analysis of Environmental Affairs Agency, Aswan branch. Wastewater sample was filtered by filter paper Whatman No.42, collected in the 1L polyethylene bottle and preserved in the refrigerator at the 5°C until the experiment.

Preparation of Sewage Sludge Adsorbents: The oven dried sewage sludge was crushed into uniform size. Chemical activators used in this experiment were 5M ZnCl₂, 3M H₂SO₄, 3M H₃PO₄, a mixture of 5M ZnCl₂ : 3M H₂SO₄ and a mixture of 5M ZnCl₂ : 3M H₃PO₄ (all mixtures in different ratios 1:1, 1:2 and 2:1 v: v).

A portion of 100 gm of the dry sludge was impregnated into 250 ml of the chemical activator for 24 h at room temperature, thereafter the supernatant liquid was removed by filtration using filter paper Whatman No. 42. The resulted active sludge was dried at 105°C for 24h and subsequently pyrolyzed at 650°C for 1h. After cooling the carbonized products that have been activated with 3M H₂SO₄ or 3M H₃PO₄ were washed with 1M NaOH solution, followed by filtration and then washed with deionized water until the pH of leached solution was between 6-7, while the sludge which activated with 5M ZnCl₂, mixture of 5M ZnCl₂ : 3M H₂SO₄, or mixture of 5M ZnCl₂ : 3M H₃PO₄ were washed with 1M HCl solution, followed by filtration and washed with deionized water until the pH of leached solution was between 6-7. The developed adsorbents ASS_{ZnCl2}, ASS_{H3PO4}, ASS_{H2SO4}, ASS_{Z:P(1:1)}, ASS_{Z:P(1:2)}, ASS_{Z:P(2:1)}, ASS_{Z:S(1:1)}, ASS_{Z:S(1:2)}, and ASS_{Z:S(2:1)} were related to activation with 5M ZnCl₂, 3M H₃PO₄, 3M H₂SO₄, 5M ZnCl₂ : 3M H₂SO₄ (1:1), 5M ZnCl₂ : 3M H₂SO₄ (1:2), 5M ZnCl₂ : 3M H₂SO₄ (2:1), 5M ZnCl₂ : 3M H₃PO₄ (1:1), 5M ZnCl₂ : 3M H₃PO₄ (1:2), and 5M ZnCl₂ : 3M H₃PO₄ (2:1) activators, respectively. The adsorbents were dried at 105 °C for 24 h, crushed and sieved to 125µm. Washing procedure by 1M HCl or NaOH solution and deionized water in the chemical activation methods were used to remove acid-soluble inorganic matter and residual activating reagent [9, 21].

Analytical Technique: The concentrations of heavy metals Cd, Pb, Cu and Mn were measured by atomic absorption spectrophotometer (AtiUnicum, mode solar - 969, UK), using hollow cathode lamps of Cd, Pb, Cu and Mn at recommended lamp current and conditions.

Absorption reading was taken at wavelength 228.8 nm for cadmium, 324.8 nm for copper, 283.3nm for lead, 279.5 nm for manganese. Air - C₂H₂ gas used as fuel gas with flow rate ranged 1.8 -2 L/min. Sample dilution ranged from 1 to 50 times. The amount of metal sorbent was evaluated by the difference between initial and remaining concentration in sample.

Batch Experiments

Leaching Test: Leaching test was done to determine the solubilization of the remaining activation reagents (H₃PO₄, ZnCl₂, H₂SO₄) and organic matters from the developed activated adsorbents. 150 mg of each developed adsorbents (ASS), with grain size 125 μm, was stirred with 50 ml deionized water for 8h at pH 5, after then the sample was filtered through Whatman filter paper No. 42. The concentration of total organic carbon, phosphorus, sulphates and zinc metal ions which released from ASS in filtrate were determined.

A Comparative Study Between the Prepared Adsorbents:

150 mg of each adsorbents (ASS_{ZnCl₂}, ASS_{H₃PO₄}, ASS_{H₂SO₄}, ASS_{Z: P (1:1)}, ASS_{Z: P (1:2)}, ASS_{Z: P (2:1)}, ASS_{Z: S (1:1)}, ASS_{Z: S (1:2)}, ASS_{Z: S (2:1)}), with grain size 125 μm, was stirred with 50 ml standard solution (30mgL⁻¹) of Cd(II), Pb(II), Cu(II) and Mn(II) for 8h. Solution pH was adjusted to 7 for Cd (II), 6 for Pb(II), 5.2 for Cu (II) and 9 for Mn (II). After 8 h the samples were filtered through Whatman filter paper No.42. The metal ion concentration in the filtrate was measured by atomic absorption spectrophotometer and the removal percent for each metal ion was calculated.

Adsorption Studies: A known weight of the best chemically activated sewage sludge adsorbent (150 mg) was mixed with 50 mL of known Cd (II), Pb (II), Cu (II) and Mn (II) concentrations. The solution was stirred for 8 h and filtered through Whatman filter paper No. 42. The metal ion concentration in the filtrate was measured by atomic absorption spectrophotometer and the removal percent for metal ion by each ASS was calculated. Effects of pH, initial metal ion concentration, contact time, adsorbent dosage and temperature of adsorption process were studied.

Morphological Studies: Several methods were used to characterize developed sewage sludge adsorbent before and after the chemical activation. The micro-morphology and chemical composition of raw and treated sludge ASS_(ZP 1:1) were examined with scanning electron microscopy dispersive (SEM-EDX), JEOL, JSM-5500LV

electron microscopy instrument at operating at five kV specimens on which a thin layer of gold or carbon had been evaporated.

Application Study on Real Wastewater Sample:

Wastewater from the laboratory for heavy metal analysis was treated with the best chemically activated sewage sludge ASS_{ZP (1:1)} at the optimum conditions for adsorption of Cd (II), Pb (II), Cu (II) and Mn (II).

RESULTS AND DISCUSSION

Leaching Test: The leaching data for the developed adsorbents are represented in Tables 2. The data are given in Table 2 shows that high concentration of Zn²⁺ (ranged 87.5 to 1.46 mgg⁻¹) leached from ASS_{Z: P (1:1)}, ASS_{Z: P (1:2)} and ASS_{ZnCl₂} adsorbents. This result renders to the using of the high concentration of ZnCl₂ (5M) reagent in the activation process. Washing of these adsorbents with 1M HCl solution is less effective to remove the excess of ZnCl₂ reagent after activation process. Yu and Zhong [21] and Calvo *et al.* [9] applied washing with 1M HCl or NaOH and distilled water in chemical and physical activation methods of adsorbents to remove acid-soluble inorganic matter and residual activating reagent.

Activated Sewage Sludge by H₂so₄ (3m), or Zncl₂: H₂SO₄ (1:1, 2:1,1:2) exhibited high leaching of SO₄²⁻ in the adsorbents ASS_{Z: S (2:1)}, ASS_{Z: S (1:2)} and ASS_{Z: S (1:1)} (49.3 to 14.6 mgg⁻¹). This result renders to the using of H₂SO₄ (3M) reagent in activation process, while all ASS which not treated by H₂SO₄ as activator exhibited low leaching of SO₄²⁻ (5.8 - 5.1 mgg⁻¹). Activation of sewage sludge by H₃PO₄ (3M), or ZnCl₂: H₃PO₄ (1:2) exhibited high leaching of PO₄³⁻ (18.2 and 2.7 mgg⁻¹, respectively); and this because the using of high ratio of H₃PO₄ (3M) reagent in activation process. Activation of sewage sludge by ZnCl₂: H₃PO₄ (1:1, 2:1) and all ASS, which not used H₃PO₄ as activator, exhibited low leaching of PO₄³⁻ (0.5 to 0 mgg⁻¹). All ASS adsorbents exhibited low leaching of total organic carbon (1.07 - 0.1 mgg⁻¹) and this resulted from the pyrolze at 650 °C. Lin and chang [22] reported that most organic carbon residue removed at 550 °C in sewage adsorbent preparation.

Comparative Study Between the Developed Adsorbents:

The adsorption data for the removal of Cd(II), Pb(II), Cu(II) and Mn(II) on the developed adsorbents [ASS_{ZnCl₂}, ASS_{H₃PO₄}, ASS_{H₂SO₄}, ASS_{Z: P (1:1)}, ASS_{Z: P (1:2)}, ASS_{Z: P (2:1)}, ASS_{Z: S (1:1)}, ASS_{Z: S (1:2)}, and ASS_{Z: S (2:1)}], at 10 mg/l initial metal ion concentrations is represented in Table 3.

Table 2: Leached amounts of Zn²⁺, SO₄²⁻, PO₄³⁻ and total organic carbon (mg/g) from chemically activated sludge adsorbents.

Adsorbents	Zn	SO ₄ ²⁻	PO ₄ ³⁻	T.Organic carbon
ASS _{ZnCl2}	87.50	5.80	0.00	1.07
ASS _{H3PO4}	0.03	49.30	0.00	0.11
ASS _{H2SO4}	0.01	5.70	18.30	0.28
ASS _{Z:P(1:1)}	1.46	23.30	0.00	0.43
ASS _{Z:P(1:2)}	0.66	34.30	0.00	0.33
ASS _{Z:P(2:1)}	8.70	14.60	0.00	0.53
ASS _{Z:S(1:1)}	0.46	5.30	0.26	0.46
ASS _{Z:S(1:2)}	0.30	5.10	2.70	0.36
ASS _{Z:S(2:1)}	5.00	5.40	0.56	0.55

Table 3: Removal percent of metals by chemically activated sludge.

Adsorbents	Removal %			
	Pb	Cd	Cu	Mn
ASS _{ZnCl2}	98.0	56.20	94.0	91.2
ASS _{H3PO4}	98.0	93.10	67.0	79.6
ASS _{H2SO4}	98.0	95.50	77.0	93.1
ASS _{Z:P(1:1)}	98.0	98.04	98.0	97.5
ASS _{Z:P(1:2)}	98.0	92.20	98.0	84.5
ASS _{Z:P(2:1)}	98.0	93.00	98.0	91.9
ASS _{Z:S(1:1)}	98.0	95.32	93.5	97.4
ASS _{Z:S(1:2)}	98.0	96.31	80.0	94.3
ASS _{Z:S(2:1)}	98.0	95.30	94.2	93.0

The data given in Table (3) show that activated sewage sludge by a mixture of (1:1) ZnCl₂: H₃PO₄ has the highest removal capability for Pb (II), Cd(II), Cu (II) and Mn (II)(98.0, 98.04,98 and 97.5%). Zhai *et al.* [24] used ZnCl₂ as chemical activator for sewage sludge and used the developed adsorbent to remove Cd (II) from aqueous solution (removal efficiency 80 %). This result disagrees with our results of ASS by ZnCl₂ (156. 2%).

Rozda *et al.* [23] prepared two types of sewage sludge-adsorbents by chemical activation with ZnCl₂ and physical activation by pyrolysis at 650 °C. The resulted adsorbents were used to remove Pb (II) from aqueous solution and ended to that chemically activated sludge with ZnCl₂ has adsorption capacity 42.9 mgg⁻¹. Carbonaceous materials with adsorptive properties were prepared from sewage sludge by chemical activation process using H₂SO₄ (1-3M) [25]. The resulted adsorbent was used to remove Cu (II) from aqueous solution, it has copper adsorption capacities varies from 77 to 83 mgg⁻¹ which are higher than our results with ASS_{H2SO4} (8.6mgg⁻¹) and ASS_{Z:S(1:1)} (38.7mgg⁻¹) adsorbents. Lian *et al.* [26] used activated sewage sludge (without chemically or physically activation) to remove Cu (II) at low concentration and indicated that the removal rate of Cu (II) is 96.47% and that result near our results by ASS_{ZnCl2}, ASS_{Z: P (1:1)}, ASS_{Z: P (2:1)}, ASS_{Z: S (1:1)}, ASS_{Z: S (1:2)} and ASS_{Z: S (2:1)} adsorbents.

Batch Adsorption Experiments

Effect of Initial Metal Ion Concentration on Adsorption:

With the increase of the initial concentration of Cd(II), Pb(II), Cu(II) and Mn(II) from 10 to75 mgL⁻¹ the removal percent of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_(ZP 1:1) adsorbent decreased from 98.3 to 95.5%, 98 to 95.9%, 93.5 to 89% and 97.4 to 94%, respectively (Fig. 1). These results showed that the highest adsorption efficiencies were at lower metal concentration; the reason may be the limited availability of active sites on the ASS surface to accommodate the high concentration of metal ions [27].

Effect of Initial pH: The removal percent Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_{ZP (1:1)} adsorbent increased with an increase of pH, the optimum pH value was pH 8 for Cd(II), pH 5 for Pb(II), pH 6 for Cu(II) and pH 9 for Mn(II) (Fig. 2).

Our result is consistent with the result obtained by Cho *et al.* [28] which reported that the Cd (II) removal increased proportionally with increasing pH from 0% at pH 3 to 95% at pH 8 by fly ash adsorbent.

Zhai *et al.* [24] used chemically activated sewage sludge for removal of Cd (II) and reported the optimum pH value for Cd (II) adsorption in the range of 5.5-6.0. Soltan [29] reported that the adsorption of Cd (II) on the surface of ores (talc, barite and chalcopyrite) increased with the increase of the pH and maximum adsorption was at pH 9. Majumdar *et al.*[30] reported maximum sorption for Pb (II) by biomass noted at pH 5 - 6. Otero *et al.* [31] showed that the maximum adsorption for Pb (II) by activated sewage sludge was at pH 4, while for Cu (II) the maximum adsorption was at pH 4. Rashed [27] showed that Pb(II) adsorption on peach and apricot stones increased as pH increases from 3 to 6.5 and the maximum adsorption of Pb(II) observed at pH 7. Bouzid *et al.* [32] showed that the Cu (II) adsorption by sewage sludge ash increased as pH increased and the maximum adsorption (99%) was at pH 7.2. Rozada *et al.*[23] and Xuejiang *et al.* [33] showed that, at pH values lower than 6.0 the removal of Cu (II) by dried activated sludge was performed by biosorption mechanism, while above pH 6 metal precipitations occurs. Taffarel and Rubio [34] reported that Mn²⁺ ion adsorption by MOCZ (Manganese oxide coated zeolite) enhances with the increase of pH medium from 4 to 8. At lower pH values, Mn²⁺ ions removal was inhibited. Stumm and Morgan [35] reported that under pH 9.6 the oxidation of Mn (II) by dissolved oxygen is very slow and low precipitation (less than 15%).

The removal of Cd (II), Pb (II), Cu (II) and Mn (II) metal ions on activated sewage sludge (ASS) are proposed as follows:

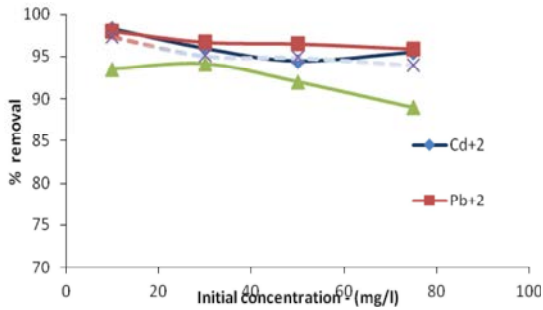


Fig. 1: Effect of initial metal concentration on the removal efficiency.

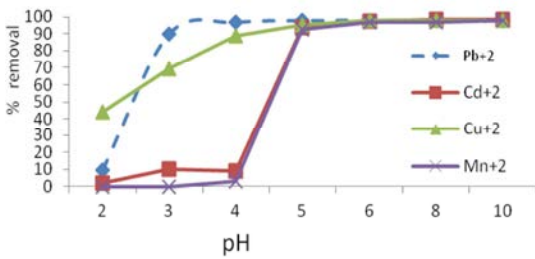


Fig. 2: Effect of pH on the adsorption of Cd²⁺, Pb²⁺, Cu²⁺, and Mn²⁺ by ASS (ZP 1:1)

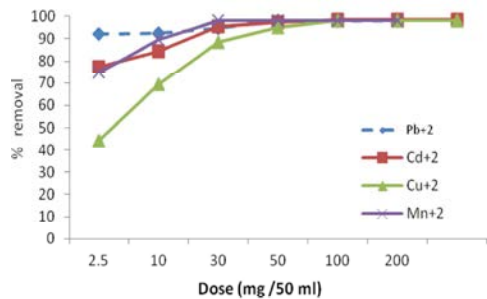
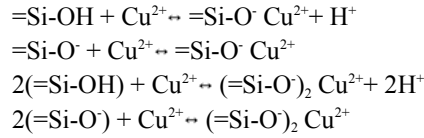


Fig. 3: Effect of ASS dosage on the adsorption of Cd, Pb, Cu, and Mn

Electrostatic Attraction: As the pH increased the activated sludge surface carried a negative charge, therefore the electrostatic attraction forces between activated sludge surface and cationic metal ion increased, that means more adsorption [6]. While poor adsorption noted at low pH value may be rendered to competition for the negatively charged binding sites of the adsorbent between metal ions and H⁺ or H₃O⁺ ions present in the solution [35, 36, 37].

Surface Complex Formation: The hydrous silicon oxide and aluminium oxide in the surface activated sewage sludge can be complex with metal ions by chemical bonding, for example, the complex reactions of Copper ion Cu (II) with hydrous silicon oxide of ASS



Precipitation Mechanism: At high pH values in the precipitation of metal ions occurred and metal ions removal enhanced. Hawari and Mulligan [38] pointed to when pH increase from 6 to 9 the solubility of metals decreases enough for precipitation to occur.

Effect of ASS Dosage on Metal Ion Adsorption: The effect of adsorbent dosage on the removal efficiency of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS (ZP 1:1) adsorbent is shown in Figure 3.

The results revealed that with increasing the adsorbent dose from 2.5 to 50 mg/50 ml the removal efficiency of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS (ZP 1:1) adsorbent increased from 77.5 to 98.4%, 92.3 to 98%, 88.5 to 97.8%, and 74.9 to 98%, respectively. This due to the availability of more surface functional groups and surface area at higher adsorbent dose [24, 37].

The optimum dosage of ASS (ZP 1:1) was 50mg/50 ml for Cd (II), Pb (II), Cu (II) and Mn (II) removal.

Zhai *et al.* [24] concluded that with the increase of ASS (ZP 1:1) adsorbent dosage the Cd (II) adsorption increase up to 10 g/l at pH 5.8. Soltan [28] showed that Cd (II) adsorption increased with increasing adsorbent dosage and the optimum dosage for Cd (II) adsorption was 1g by talc, barite and chalcopyrite. Ahmad *et al.* [39] reported that Pb (II) adsorption increased with an increase in the dose of sawdust, at pH 7, from 0.25 to 2 g and resulted in an increase of Pb (II) adsorption from 90.4 to 93.9%. Hammami *et al.* [20] observed that variation of the sorption capacity for Pb (II), Cd (II) and Cu (II) versus activated sludge (biomass) concentration was steady or decreased with biomass concentration due to the screen effect between cells (a block of the cell active sites). Lian *et al.* [26] reported that the increasing of activated sewage sludge dosage from 1 to 6 g has little effect on Cu (II) removal, at the optimum dosage of ASS 3g /100 ml, Cu (II) removal was 96.4% (0.27 mg/g). Ozdemir *et al.* [40] (showed that the adsorption capacity of Cu(II), Cd(II) and Mn(II) decreased with increasing dry mass concentration, despite increases in metal removal (biosorbed metal%) at pH 4, 6 and 5, respectively. Taffarel *et al.* [34] reported that Mn (II) adsorption enhanced from 42 to 99% by manganese oxide coated zeolite when the adsorbent dosage increased from 1 to 6 g/L.

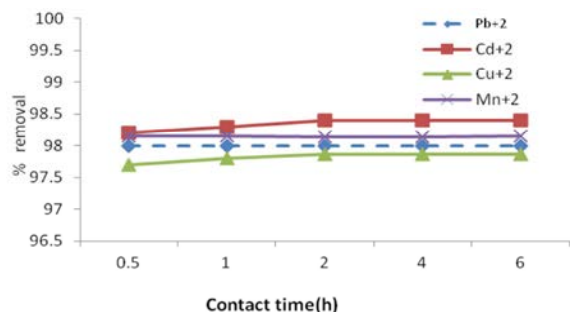


Fig. 4: Effect of contact time on the adsorption of Cd, Pb, Cu, and Mn.

Effect of Contact Time on Metal Ion Adsorption: Adsorption of 10 mg L^{-1} Cd (II), Pb (II), Cu (II) and Mn (II) on ASS_(ZP 1:1) was studied as a function of contact time in order to obtain a suitable equilibrium time (Fig. 4).

The results showed that after 30 min the removal of Cd(II), Pb(II), Cu(II) and Mn(II) adsorption was 90%, while one hour as a contact time was enough to achieve maximum adsorption for metal ions on the surface of ASS_(ZP 1:1). It can be concluded that Cd(II), Pb(II), Cu(II) and Mn(II) were adsorbed onto ASS_(ZP 1:1), very rapidly within 30- 60 minutes. The fast adsorption at the initial stage may be due to the higher driving force making fast transfer of metal ions to the surface of adsorbent particles and the availability of the uncovered surface area and active sites on the adsorbent, with increasing time the availability of the uncovered surface area and the remaining active sites decreased [41, 42].

Our results nearly similar to the results obtained by Gurgel *et al.* [43]. The adsorption of Cd(II), Pb(II), and Cu(II) ions by chemically modified-sugar cane bagasses increases with contact time and the equilibrium time was achieved after 10 - 20 min. Gupta *et al.* [44] reported that 90% removal of Cd(II) and Ni^{2+} by bagasse fly ash is possible in about 60 min. Lian *et al.* [26] observed little effect of contact time on Cu(II) adsorption by activated sewage sludge, Cu(II) adsorption reached up to 90% after 0.5 h. For Cd (II) removal of 96% Cd (II) was after 7 h. Rashed [27] reported that Pb^{2+} adsorption on peach and apricot stones increased with time to reach its maximum adsorption at 3 and 4 h, respectively. Fonseca *et al.* [45] reported that the equilibrium time for Mn (II) and Cd (II) by a clay mineral are 48 and 72 h, respectively, (long time to achieve the adsorption).

Effect of Solution Temperature on Metal Ion Adsorption: The solution temperature has two main effects on the adsorption process, the temperature can affect the

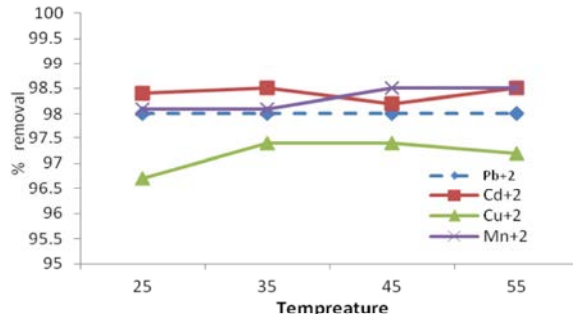
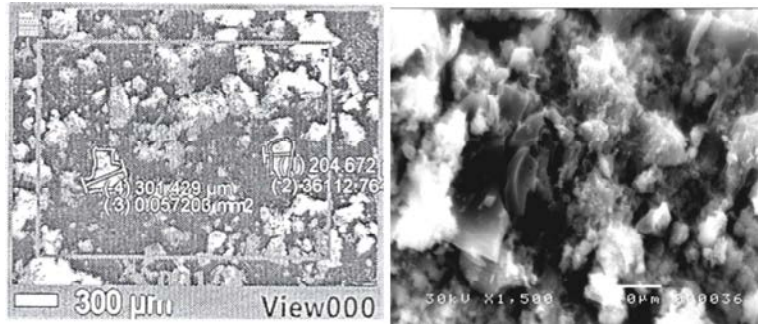


Fig. 5: Effect of solution temperature on the adsorption of Cd, Pb, Cu, and Mn.

diffusion rate of the sorbate within the pores as a result of decreasing solution viscosity [46] and the temperature can affect the number of the sorption sites generated because of breaking of some internal bonds near the edge of active surface sites of sorbent [47].

The results from Fig.5 showed that with the increase of solution temperature from 25 to 35 °C adsorption of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_(ZP 1:1), increase and after then the adsorption decrease. This could be due to the strength of the binding and attraction between metal ions and active site on the surface of ASS_(ZP 1:1), where the decrease in adsorption with the rise of temperature may be due to the weakening of adsorptive forces between the active sites of the adsorbents and adsorbate species and also between the adjacent molecules of the adsorbed phase [48]. Lian *et al.* [26] observed that the biosorption of Cu (II) by activated sewage sludge maintains maximum (94%) when temperature changes from 10 to 40 °C, while the biosorption of Cd (II) is exert a little increasing with temperature increasing. Ozdemire *et al.* [40] reported that no significant change in Mn(II), Cd(II) and Cu(II) adsorption by dried powdered cell (microbial cells) when the temperature increase from 30 to 80 °C. Xuejiang *et al.* [33] reported that the sorption capacities of Cu (II) and Pb (II) by activated sewage sludge decreased with the increase of solution temperature which indicates an exothermic reaction.

Characterization of Sewage Sludge and Developed Adsorbents: The surface structure of developed adsorbents ASS_(ZP 1:1) before and after chemical activation was analyzed by scanning electronic microscopy (SEM). The textural structure examination of sample particles can be observed from the SEM photographs at 430 magnifications (Fig.6 and Table 4).



(a) Raw sewage sludge.

(b) Adsorbent ASS (ZP 1:1).

Fig. 6: SEM of raw sewage sludge and developed adsorbent of ASS (ZP 1:1).

Table 4: chemical composition of ASS_(ZP 1:1) adsorbent.

	Elements Mass %											
	Na	Cl	Al	Si	Ti	P	S	Ca	Fe	Cu	Zn	K
ASS _(ZP 1:1)	20.15	0.61	2.27	12.48	0.32	17.54	0.92	4.12	3.40	0.13	37.72	0.33

The scanning electron microscope (SEM) of sewage sludge before and after activation is shown in Fig.6. Raw and adsorbent sewage sludge seems as brown color particles. The dried particles in raw sewage sludge used as precursor are irregular spherical (Fig. 6a). The materials resulting from activation (adsorbent) shows the breakdown of the granules, also particle appears in a porous structure with a wide range of pore sizes (Fig.6b). The data in Table 4 showed that the main chemical composition of ASS_(ZP 1:1) is silica, phosphorous and zinc and sodium in addition to a small percent of iron and aluminium.

Adsorption Isotherms: Langmuir, Freundlich and Scatchard isotherms were applied to describe the sorption equilibrium of metal ions on adsorbent. The Freundlich expression is an empirical equation based on a heterogeneous surface, which relates that the concentration of a solute on the surface of an adsorbent, to the concentration of the solute in the liquid, Freundlich equation is given as follow:

$$q_e = K_{fc} C_e^{1/n} \quad (1)$$

Eq. (1) can also be expressed in the linearized logarithmic form

$$\text{Log } q_e = \text{Log } k_f + (1/n) \text{Log } C_e \quad (2)$$

Where q_e is the amount adsorbed (mg/g), C_e is the equilibrium concentration of the adsorbate (mg/l) and k_f and n are the Freundlich constants related to adsorption

capacity and adsorption intensity respectively. When $\text{Log } q_e$ is plotted versus $\text{Log } C_e$, the slope is equal to $(1/n)$ and the intercept is equal to $\text{Log } k_f$. The high value of R^2 (Correlation coefficient of the line) indicates that the adsorption follows Freundlich isotherm model perfectly [50]. When the value of $1/n$ is between 0 to 1 indicate the heterogeneity of the sorbent [51], furthermore, the smaller $1/n$ and larger K_f values for sorbent indicate that sorbent has higher adsorption capacity, intensity and affinity for metal ion than the other types of sorbents [52].

The Langmuir describes monolayer sorption which assumes that sorption occurs at specific homogeneous sites on the adsorbent [53]. Langmuir equation expressed as follows

$$C_e / q_e = C_e / Q_o + 1 / Q_o b \quad (3)$$

Where C_e (mg/l) is equilibrium concentration, q_e (mg/g) the amount adsorbed at equilibrium, b (L/mg) is the Langmuir constant which related to the affinity of the binding site and Q_o (mg/g) the capacity parameter, when C_e / q_e is plotted versus C_e , the slope is equal to $(1/Q_o)$ and the intercept is equal to $1/Q_o b$.

The Scatchard plot analysis is a widely used technique in evaluating the main interaction types taking a role in a particular sorption process and dependence of binding types to experimental conditions, the Scatchard isotherm represents intermediate situations close to the Langmuir model. The shape of Scatchard plot is related to the type of the interactions of analyte with the adsorbent. The presence of a deviation from linearity on a plot based on Scatchard analysis usually points out the presence of more than one type of the binding sites. Whilst the linearity of the Scatchard plot indicates that the binding sites are identical and independent. So, if the Scatchard plot is linear with a negative slope, it is related to interaction between the analyte and the b binding sites

Table 5: Langmuir, Freundlich and Scatchard isotherm constants for adsorption of Cd, Pb, Cu and Mn by ASS_(ZP 1:1).

Metalion	Langmuir constants			Freundlich constants			Scatchard constants		
	Q ^o	b	R ²	1/n	K _f	R ²	K _s	Q _s	R ²
Cd	32.89	0.4537	0.7143	0.619	9.40	0.973	0.546	31.3	0.586
Pb	47.84	0.3055	0.838	0.736	10.432	0.9972	0.36	42.8	0.747
Cu	42.37	0.138	0.942	0.767	4.978	0.964	0.12	46.2	0.763
Mn	41.84	0.252	0.8225	0.693	8.009	0.994	0.083	32.9	0.713

Table 6: Removal percent of metal ions (Cd, Pb, Cu and Mn) in lab wastewater after treatment with ASS_(ZP 1:1)

Sorbent	Removal percent %			
	Cd	Pb	Cu	Mn
ASS _(ZP1:1)	90.80	97.60	82.40	85.60

follow the Langmuir model. When the Scatchard plot exhibits a deviation from linearity the interaction follows the analysis of data in terms of the Freundlich model [55]. The Scatchard isotherm equation for a linear plot [56] is represented by the following equation:

$$q_e c_e = K_s (Q_s - q_e) \quad (4)$$

Where Q_s and K are Scatchard constants related to the maximum monolayer adsorption capacity and equilibrium adsorption constant, respectively.

The results obtained on the adsorption of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_(ZP1:1) at different initial metal ion concentrations (10, 30, 50 and 75 mgL⁻¹) were analyzed by the well know models given by Freundlich, Langmuir and Scatchard.

The values of R² for Langmuir, Freundlich and Scatchard isotherms in Table (5) indicated that Freundlich model fits better for Cd (II), Pb (II), Cu (II) and Mn (II) than the Langmuir model. From Freundlich constants, the values of 1/n for adsorption on ASS (ZP 1:1) were 0.619 for Cd (II), 0.736 for Pb (II) 0.767 for Cu (II) and 0.693 for Mn (II). The previous values of 1/n is between 0 - 1 which revealed that the heterogeneity of ASS_(ZP 1:1) surface.

From Scatchard parameters the values of R² for adsorption on ASS_(ZP1:1) were 0.586 for Cd (II), 0.747 for Pb (II) 0.763 for Cu (II) and 0.713 for Mn (II). The previous values of R² are revealed that the Scatchard plots exhibited a deviation from linearity which pointed to the presence of more than one type of the binding sites.

Application Study on Real Wastewater Samples: The possibility of the utilization of ASS_(ZP 1:1) as an effective adsorbent for the removal of Cd(II), Pb(II), Cu(II) and Mn(II) was studied by the application on real wastewater sample (Lab wastewater) containing these metals. The

concentrations of metal ions in the Lab wastewater sample before and after the treatment with ASS_(ZP 1:1) are represented in Table 6.

Previous results revealed that the possibility of the utilization of ASS_(ZP 1:1) adsorbent as an effective adsorbent for the removal of Cd(II), Pb(II), Cu(II) and Mn(II) from polluted water.

CONCLUSIONS

Activated sewage sludge by a mixture of ZnCl₂: H₃PO₄ (1:1) was the best activator for the removal of Cd(II), Pb(II), Cu(II) and Mn(II) from wastewater. The adsorbent obtained by chemical activation with ZnCl₂: H₃PO₄(1:1) is novel finding. From leaching test data of the developed adsorbent it is concluded that the type and the concentration of chemical activator and the washing process after activation have an important role in preparation of adsorbent. The initial metal ion concentration, pH value and dosage of ASS_(ZP 1:1) adsorbent showed significant effect on the adsorption process of Cd(II), Pb(II), Cu(II) and Mn(II) by ASS_(ZP 1:1). The optimum pH value was pH 8 for Cd(II), pH 5 for Pb(II), pH 6 for Cu(II) and pH 9 for Mn(II). The optimum initial metal concentration and dosage of ASS_(ZP 1:1) was 10 mgL⁻¹ and 1gml⁻¹, respectively. Contact time and solution temperature exhibited little effect on the adsorption process which reached equilibrium after one hour. The adsorption data of Cd (II), Pb (II), Cu (II) and Mn (II) on ASS_(ZP 1:1) fitted well the Freundlich model. ASS_(ZP 1:1) can be used as an effective adsorbent for the removal of Cd (II), Pb (II), Cu (II) and Mn (II) from polluted water.

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