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A theoretical overview of heavy metal treatment with agricultural wastes

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Abstract

Tomato plant between Pb^{2+}, Cd^{2+} with tomato waste having amino and the other functional groups waste contain cellulose materials(lignin), polysaccharides having functional groups having the ability of binding heavy metals as sorbents is commonly cultivated plant for its fruits. Aim of this study to determine the best alternative way to search the binding capacity of agricultural waste as theoretical to remove heavy metals with tomato plant from waste waters as economically by comparing experimental results respectively. The capacities of adsorption for heavy metals (Pb(II), Cu(II) and Cd(II)) of the tomato plant residue were 0.092, 0.533 and 0.238 mmol/g sorbent. As theoretical, HF (Hartree-fock), lanl2dz methods were used for molecular calculation. The theoretical calculations were carried out by means of the lanl2dz functional base. The chemical activities were calculated by using this method. The removal of Pb^{2+} and Cd^{2+} found lower than Cu^{2+} because of the strong complex formation as experimental and theoretical calculations supported this issue. Theoretical calculations are important to prevent loss of time and cost.

Keywords: Pb(II), Cu(II) ,Cd(II), biomass,HF, docking, heavy metals

1. INTRODUCTION

Solid waste management is an important system because of involving multiple subsystems inputs, materials and resources to process waste properly [1]. The role of ecosystems in decreasing the effects of common agricultural wastes is recognized in several trimmer measures and public policy attempts in many parts of the world [2]. Heavy metals are hazardous substances to the human body, animals and plants because they accumulate in the cells of them. They are used a lot of industrial activities for example, battery manufacturing, electroplating, mine-processing, production of paint and fertilizer materials, etc. When the acid rain reaches the soil, some heavy metals go into ground water, lakes and rivers. Moreover the heavy metals of industrial wastes with soil and then the water reaches to the living organisms and they are taken into the human body with the consumption products from soil and drinking water [3-7].

Some of the heavy metals is lead, copper and cadmium. Lead is one of the hazardous heavy metal to the living organisms. If it gets into human body, it causes harmful effects. For example; ıt can damage red blood cells and decrease the ability of carrying oxygen to the tissues. It is also harmful for nerves system and kidneys. Especially, young children and babies are at the risk of lead poisoning. Lead is the main inhibitor of some enzymes as well [8,9].

The other hazardous heavy metal for living organisms is Cadmium. The mainly used industrial areas are cadmium-nickel batteries, mining alloys, pigment and fertilizers. The harmful effects of the human body are acute and chronic metabolic disorders such as renal damage, hypertension and emphysema [8]. Copper is commonly used heavy metal in industrial areas such as electrical products and also highly found as industrial wastes. Intaking of the required quantitative is essential

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but excessive of have toxicity to the human body such as itching, dimerization and soles of feat [10,11].

The notification of effecting heavy metal ions to the living organisms, the water quality is the important to focus on. Many methods, chemical and physical, of have been used for the elimination of heavy metals from polluted waters with the industrial wastes. Chemical precipitation, filtration, ion-exchange, electrochemical treatments, coagulation, evaporation, membrane separation are some of them [12-16]. These methods have some disadvantages. For example, the chemical precipitation; chemical substances are costly and poor recovery heavy metals [17,18]. The most applicable alternative method is biosorption because it has high efficiency and economically to purify waste water [19-22].

In recent years, natural harvested agricultural biomaterials have been used to remove heavy metals from polluted waters as sorbent due to low operating cost, relative abundance, specific selectivity of metal interest and not having the other compounds. Some of the biosorbents is rice husk [23],tobacco steam, pine bark [24] ,moringa oleifera [25],saw dust [26], cashew nut shell [27], cork biomass [28],barley straw [29], lignin [30], loquat bark [31] and tomato waste [32] .The new method should be cheap and save up time.

In the functional groups of tomato residues are determined with using FTIR (Fourier transform infrared spectroscopy) by Goatha et al. And also the functionals groups of tomato plant waste, metal binding are shown in Fig 1 [32] by them. The using of tomato plant residues is preferred due to not having commercials values, simple preparation and the local availability [32].

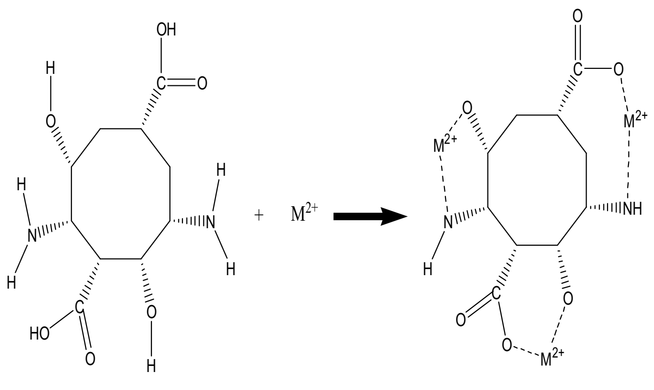

Figure 1. Schematic diagram of functional groups and metal binding on tomato

Tomato has been cultivated commonly for its fruits. After harvesting, the residues of tomato plant are generally burned and not having commercial value. They contain cellulose materials (lignin), polysaccharides that have functional groups having the ability of binding heavy metals as sorbents [33,34]. Because of having many functional groups and strong metal affinity, they are preferred to instead of the expensive synthetic biosorbents [35-37]. In this study; the best alternative way will be determined to search the binding capacity of agricultural waste as theoretical to remove heavy metals with tomato plant from waste waters as economically by comparing experimental results respectively. Make justified all lines as we do in this style guide.

2. EXPERIMENTAL

2.1. Materials and method

In this study; Pb(II), Cu(II), Cd(II) were used as the heavy metal ions. The metal ion solutions were firstly are taken 1000 mg/L after that they were prepared for atomic absorption standard stock metal solution as the water down to the necessary concentrations (100 mg/L).

The dried tomato plant residues were collected waste forms from the field of Laçin, the village of Eskişehir in Turkey, washed three times with distilled water, dried at 60-80 ^oC overnight and turned into particles, as a sorbent. After putting them into plastic bottles, 0.05 g the dilutions were made for the required concentrations (100 mg/L).

The sample was shaken at 125 rpm at 25 ^oC for about 2 h. The content mixture was centrifuged for 10 min. The concentrations of Pb(II), Cu(II), Cd(II) in mixture were analyzed by using AAS (Atomic absorption spectroscopy). The amount of biosorbed metal ions to per grams of biomass was calculated this equitation: [38,45].

$$q=(Ci-Ceq)\ V/m \qquad (1)$$

q (mg/g)
Ci (Initial concentration (mg/L)
Ceq (Equilibrium concentration (mg/L)
V (Volume of the medium (L)
m (Amount of biomass (g)

3. THEORETICAL

3.1.Materials and method

The electronic structures of tomato-heavy metals complex are observed by HF, lanl2dz methods and it was used for geometry optimization. The theoretical calculations were performed by means of the lanl2dz functional. The theoretical values were obtained by using the result of HF method [39,40]. The structure activity of the compounds using this method were indicated and appraised.

4. RESULTS AND DISCUSSION

4.1.Experimental

The biosorption capacities of the tomato plant waste for the selected heavy metals Pb(II), Cu(II) and Cd(II) were 0.092, 0.533 and 0.238 mmol/g sorbent, respectively, in dried tomato biomass waste at pH=7 (approximately) and at 25 °C. The adsorption competitions of all the heavy metal ions were the evident of degree of the metal uptakes in dried tomato biomass waste. Initially, the heavy metal concentrations, the metal sorption capacity of Cu(II) among three heavy metals was the highest in tomato plant biomass waste. On the other hand, the metal loadings order were Cu(II)> Cd(II)> Pb(II) from high to low.

The differences capacity of adsorption for the selected metals is possibly related to the electronegativities of the cations [46]. To comprehend of the binding sites on the biomass (tomato waste) surface, a thermodynamic model (HF includes lanl2dz base) could be improved by explaining of the capacity of the active metal ion adsorption sites on the surfaces of the tomato plant waste to indicate the binding ability of heavy metal ions on the surface of the biomass such as adsorption and coagulation.

As a not common commercial agricultural and natural cellulosic biomass, tomato plant waste is a complex materials having cellulose materials (lignin), hemicellulose and polysaccharides as the mainly compounds. These compounds ordinarily have more polar functional groups, as amines, alcohols, carboxylic acids and phenolic hydroxides. The polar functional groups mentioned above may participate to get the existing of the charged sites on the surfaces of biomass [32,41]. It may be partly taking into account for the capability of the biomass to catch cations in stability compose by forces such as, coulombic, electrostatic forces and covalent bonding forces of some these cations. The biomass surface charge also plays an important role in electrostatic adsorption on the biomass of tomato. Shortage of fresh water is serious problem for many regions. A lot of various desalination technologies is used to solve this problem [42]. One of them is biosorption.

4.2. Theoretical

The Gibbs Free Energy of Tomato+Cu^{2+}, Tomato+Pb^{2+} and Tomato+Cd^{2+} are given in Table 1(The values are given as Hartree;1Hartree:=627.5095 kcal. mol^{-1}).

Table 1 The Gibbs Free Energy of tomato waste with heavy metals

HF(lanl2dz (Separately)	ΔG Hartree	DFT (Together) Hartree	ΔG Hartree	ΔG(Difference) Hartree
Tomato+Cu^{2+}	-1064.22072	Tomato-Cu^{2+}	-1458.42860	-394.20788
Tomato+Pb^{2+}	-873.16663	Tomato-Pb^{2+}	-885.467470	-12.30084
Tomato+Cd^{2+}	-916.01128	Tomato-Cd^{2+}	-1012.93612	-96.92484
Tomato	-869.22643			

The values of Gibss free energy (difference) from Table 1 are -394.20788, -96.92484 and -12.30084 Hartree. The order from high to low is Tomato-Cu^{2+}>Tomato-Cd^{2+} > Tomato-Pb^{2+}. The experimental sorbent capacity is the same order with these theoretical values. Cheng et al. emphasized that the negative value of ΔG° of Pb(II) ion and the decreasing value of ΔG° proved that the adsorption process was spontaneous and more favorable [43]. In our study; The theoretical calculations are supported with the experimental results of Cheng et al [43].

HOMO (highest occupied molecular orbital),LUMO (lowest unoccupied molecular orbital), Δ(HOMO-LUMO) and dipole moments of Tomato+Cu^{2+}, Tomato+Pb^{2+} and Tomato+Cd^{2+} are given in the Table 2.

Table 2 HOMO,LUMO, Δ (HOMO-LUMO) and dipole moments of tomato waste with heavy metals

HF(lanl2dz (Separately)	HOMO (eV)	LUMO (eV)	Δ(LUMO-HOMO) (eV)	Dipol moment (Debye)
Tomato-Cu^{2+}	-0.54534	-0.32153	0.22381	8.40750
Tomato-Pb^{2+}	-0.56831	-0.12208	0.44623	8.08420
Tomato-Cd^{2+}	-0.46981	-0.23527	0.23454	7.25880
Tomato	-0.55075	-0.04849	0.50190	10.20100

HOMO-LUMO differences indicates the stability of compounds; The comparing values of the stability of tomato-heavy metals (Cu(II), Pb(II), Cd(II)) complex from the Table 2 are 0.22381, 0.44623, 0.23454 eV**.** The order from high to low is Tomato- Pb^{2+} >Tomato-Cd^{2+}> Tomato-Cu^{2+}. Tomato-Pb^{2+} complex is more stable than the others. In this experimental study, the mixture of tomato residue and metal, Pb^{2+} cations remained on the biosorbent of tomato residue due to the stability of complex as shown in theoretical calculations.

The results of LUMO order in Table 2: Tomato-Cu^{2+}>Tomato-Cd^{2+}>Tomato-Pb^{2+};-0.32153,eV -0.12208 eV and -0.23527 eV. The experimental results are also the same order. Electron affinity (A) is determined the energy of a molecule after added one e-.

$A= -E_{LUMO}$

In Table 2; the electron affinity of tomato waste is -0.04849 eV and the others are given above. The electron affinity increases with the complexion of Cu^{2+}, Cd^{2+} and Pb^{2+}.

Docking results of Tomato+Cu^{2+}, Tomato+Pb^{2+} and Tomato+Cd^{2+} are given in the Table 3.

Table 3 Total binding energy of tomato waste with heavy metals by using docking

Docking Results	E total
Tomato-Cd	-39.01
Cd $^{2+}$-tomato-Cd	-43.83
Tomato -Cu	-38.34
Cu $^{2+}$- tomato -Cu	-30.63
$CuSO_4$- tomato -Cu	-29.25
Tomato--Pb	-38.34
Pb_2- tomato -Pb	-43.85
$PbNO_3$- tomato -Pb	-46.89

The removal of Pb $^{2+}$ and Cd $^{2+}$ found lower than Cu $^{2+}$ because of the strong complex formation between Pb^{2+},Cd^{2+} with tomato waste and docking results are also supported this issue as seen in Table 3.

Setyono and Valiyaveettil indicated that the desorption efficiencies of heavy metal ions, especially Ni^{2+}, Cd^{2+}, and Cr(VI) were lower than Cu^{2+} due to strong complexation with amine groups of functionalized paper [44]. The thermodynamics values of Pb(II) adsorption onto the tobacco stems shown that the adsorption was spontaneous and endothermic [45]. In this study; the quantity of removal Cd^{2+} was also lower than Cu^{2+} as the experimental and theoretical calculations supported this issue. So, we can assume that the removal of Pb^{2+} and Cd^{2+} is lower than Cu^{2+} because of the strong complex formation between Pb^{2+},Cd^{2+} with tomato waste due to be having amino and the other functional groups.

5. CONCLUSIONS

In this experimental and theoretical study, the heavy metals binding efficiency of tomato plant waste was investigated and the indicated result can be reached; The tomato plant waste exhibited a strong binding capacity for the heavy metals as being calculated in this study; Pb(II), Cu(II) and Cd(II), with respective equilibrium loadings of 19.06, 33.87 and 26.76 mg of metal per g of biosorbent. Theoretical calculations are applied the other heavy metals and agricultural wastes due to be supported experimental results as mentioned above.

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REFERENCES

[1] Chifari R, Piano SL, Matsumoto S. Tasaki T. “Does recyclable separation reduce the cost of municipal waste management in Japan?” Waste Management., 2017.
[2] Balestrinia R, Sacchib E,Tidilia D, Delcontea CA, Buffagnia A. “Factors affecting agricultural nitrogen removal in riparian strips: Examples from groundwater-dependent ecosystems of the Po Valley (Northern Italy) Agriculture”, Ecosystems and Environment, 221, 132–144, 2016.
[3] Soylak M, Elci L, Dogan M. “Flame atomic absorption spectrometric determination of cadmium, cobalt, lead and nickel in chemical grade potassium salts after an

enrichment and separation procedure” Journal Trace Microprobe Technology 17,149–156, 1999.
[4] Kazi TG, N. Jalbani, N. Kazi, MB. Arain, MK. Jamali HI. Afridi GA. Kandhro, RA. Sarfraz, AQ. Shah, R. Ansari. “Estimation of toxic metals in scalp hair samples of chronic kidney patients,” Biological Trace Element Research 127,16–27, 2009.
[5] Afridi HI. TG. Kazi, NG. Kazi, MB. Arain, N. Jalbani, RA. Sarfraz, AQ. Shah, JA. “Evaluation of arsenic, cobalt, copper and manganese in biological samples of steel mill workers by electrothermal atomic absorption spectrometry” Baig, Toxicology and Industrial Health 25, 59–69, 2009.
[6] Arain MB, TG. Kazi, MK. Jamali, N. Jalbani, HI. Afridi, Shah, A. “Total dissolved and bioavailable elements in water and sediment samples and their accumulation Oreochromis mossambicus of polluted Manchar Lake”, Chemosphere 70, 1845–1856, 2008.
[7] Gupta VK. A. Rastogi, Nayak, A. “Biosorption of nickel onto treated alga (Oedogonium hatei): Application of isotherm and kinetic models” Journal of Colloid and Interface Science342,533–539, 2010.
[8] Zhu C , Z. Luan, Y. Wang, Shan, X. “Kinetic and isothermal studies of lead ion adsorption onto bentonite”, Separation and Purification Technology. 57, 161–169, 2007.
[9] King P, N Rakesh, S. Beenalahari, Y.P. Kumar, Prasad, VSRK. “Removal of lead from aqueous solution using Syzygium cumini L.: equilibrium and kinetic studies”, Journal of Hazardous Materials. 142,340–347, 2007.
[10] Huang YH, CL. Hsueh, HP. Cheng, LC. Su, Chen CY. “Thermodynamics and kinetics of adsorption of Cu(II) onto waste iron oxide”, Journal of Hazardous Materials. 144,406–411, 2007.
[11] Al-Asheh S, N. Abdel-Jasou Barat, F. “Packed bed sorption of copper using spent animal bones: factorial experimental design, desorption and column regeneration”, Advances in Environmental Research. 6, 221–227, 2002.
[12] Naushad M. “Surfactant assisted nano-composite cation exchanger: Development, characterization and applications for the removal of toxic Pb $^{2+}$ from aqueous medium”, Chemical Engineering Journal, 235, 100–108, 2014.
[13] NaushadM, Z.A. A.,Othman Islam M. “Adsorption of Cd 2+ ion using a new composite cation-exchanger polyaniline Sn(IV) silicate: Adsorption kinetics and thermodynamic studies”, International Journal of Environmental Science and Technology,10,567–578, 2013.
[14] Bhattacharyya KG. . Gupta, SS. “Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review”, Advances in Colloid and Interface Science 140, 114–131, 2008.
[15] Puanngam M, Unob F. “Preparation and use of chemically modified MCM-41 and silica gel as selective adsorbents for Hg(II) ions,” Journal of Hazardous Materials. 154, 578–587, 2008.
[16] Jiang MQ, XY. Jin XQ. Lu Chen ZL. “Adsorption of Pb(II), Cd(II), Ni(II) and Cu(II) onto natural kaolinite clay,”Desalination 252, 33–39, 2010.
[17] Kadiverlu K, K Thamaraiselvi, Namasivayam C. “Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste”, Bioresource Technology 76-1, 63-65, 2001.
[18] Sandau E, Sandau P, Pulz O. “Heavy metal sorption by microalgae.” Acta Biotechnology 16, 227–235, 1996.
[19] Yang D, J. Debing G. Huili Z. Lianbi Xiaosong, Y. “Biosorption of aquatic cadmium(II) by unmodified rice straw”, Bioresource Technology. 114, 20–25, 2012.
[20] Davis TA, Volesky B, Vieira RHSF. “Sargassum seaweed as biosorbent for heavy metals” Water Research 34-17, 4270-4278, 2000.
[21] Demir A, Arisoy M. “Biological and chemical removal of Cr(VI) from waste water: cost and benefit analysis”, Journal of Hazardous Materials 147, 275-280, 2007.
[22] Esposito A, Pagnanelli F, Lodi A, Solisio C Vegliö F. “Biosorption of heavy metals by Sphaerotilus natans: an equilibrium study at different pH and tobacco dust biomass concentrations”. Hydrometallurgy, 60, 129-141, 2001.
[23] Ajmal M, RAK. Rao JA. Anwar Ahmad R. “Adsorption studies on rice husk: removal and recovery of Cd(II) from wastewater”Bioresource Technology 86, 147–149, 2003 .
[24] Al-Asheh S, Duvnjak, Z.“Binary metal sorption by pine bark: study of equilibria and mechanisms”, Separation Science and Technology 33 (9), 1303–1329, 1998.
[25] Reddy DHK , DKV. Ramana K. Seshaiah Reddy, AVR. “Biosorption of Ni(II) from aqueous phase by Moringa oleifera bark, a low cost biosorbent”, Desalination 268, 150–157, 2011.
[26] Bulut Y, Tez Z. “Removal of heavy metal from aqueous solution by sawdust adsorption”, Journal of Environmental Sciences 19 (2), 160–166, 2007.
[27] Kumar PS, S. Ramalingam S.D. Kirupha A. Murugesan T. Vidhyadevi Sivanesan S. “Adsorption behavior of nickel(II) onto cashew nut shell: Equilibrium, thermodynamics, kinetics, mechanism and process design”, Chemical Engineering Journal 167, 122–131, 2011.
[28] Chubar N, JR. Carvalho Correia MJN., “Cork biomass as a biosorbent for Cu(II), Zn(II) and Ni(II),” Colloids and Surfaces A: Physicochemical and Engineering Aspects 230, 57–65, , 2004.
[29] Thevannan A, R. Mungroo, Niu CH. “Biosorption of nickel with barley straw”, Bioresource Technology. 101, 1180–1776, 2010.
[30] Srivastava S, A. Singh Sharma A. “Studies on the uptake lead and zinc by lignin obtained from black licor—a paper industry waste material“Environmental Technology 15, 353–361, 1994.

[31] World Health Organization (WHO), Guidelines for Drinking-water Quality, World Health Organization, Geneva,..595, . 2006.
[32] Gutha Y, VS. Munagapati M. Naushad & Abburi K. “Removal of Ni(II) from aqueous solution by Lycopersicum esculentum (Tomato) leaf powder as a low-cost biosorbent” Desalination and Water Treatment 54, 200–2081, 2015.
[33] Babel S, Kurniawan TA. “Low-cost adsorbents for heavy metalsuptake from contaminated water: a review” Journal of Hazardous Materials, B-97, 219-243, 2002.
[34] Brown PA, Gül SA, Ailen SJ. “Metal removal from wastewaterusing peat.” Water Research 34-16, 3907-3916, 2000.
[35] Pagnanelli F, Trifoni M, Beolchini F, Esposito A, Toro L, VeglioF. “Equilibrium biosorption studies in single and multi-metal systems,” Process Biochemistry, 37, 115–124, 2001.
[36] Sheth KN, Soni V., “Comparative study of removal of Cr (VI) with PAC, GAC and adsorbent prepared from tobacco stems”, Journal of Industrial Pollution Control 20, 45–52, 2004.
[37] Pehlivan E, BH Yanik G. Ahmetli Pehlivan M. “Equilibrium isotherm studies for the uptake of cadmium and lead ions onto sugar beet pulp”, Bioresource Technology 99, 3520–3527, 2008.
[38] Areco MM, Hanela S, Duran J, Afonso M.S. “Biosorption of Cu(II), Zn(II), Cd(II) and Pb(II) by dead biomasses of green alga Ulva lactuca and the development of a sustainable matrix for adsorption implementation”, Journal of Hazardous Materials 213– 214, 123– 132, 2012.
[39] Gökalp F. “A Study on Piperine, Active Compound of Black Pepper”, APJES IV-III, 29-32, 2016.
[40] GökalpF. “A study on the chemical properties of eugenol and eugenol acetate, clove essential oils,” Sigma Journal of Engineering and Natural Sciences 34 (3 407-414, .), 2016.
[41] Matis KA, Zouboulis AI, Grigoriadou AA. Lazaridis, NK. Ekateriniadou L.V. “Metalsorption-flotation. Application to cadmium removal” Applied Microbiology and Biotechnology, 45, 569- 573, 1996.
[42] WuT, Wang G, Dong FZQ, Ren Q. Wang J, Qiu J. “Surface-treated carbon electrodes with modified potential of zero charge for capacitive deionization”,Water Research 93, 30-37, 2016.
[43] Cheng Y, Yang C, He H, Zeng G, Zhao K, Yan Z. “Biosorption of Pb(II) Ions from Aqueous Solutions by Waste Biomass from Biotrickling Filters: Kinetics, Isotherms, and Thermodynamics,” Journal of Environmental Engineering, Eng142(9) 1—1, 2016.
[44] Setyono DS. “Functionalized paper—A readily accessible adsorbent for removal ofdissolved heavy metal salts and nanoparticles from water, Valiyaveettil,” Journal of Hazardous Materials, 302; 120–128, 2016.
[45] Li W, L. Zhang J. Peng N. Li S. Zhang, Guo S. “Tobacco stems as a low cost adsorbent for the removal of Pb(II) from wastewater: Equilibrium and kinetic studies” Industrial Crops and Products 28, 294–302, 2008.
[46] By Ma. del Rosario M. V., Omar F. G.V., Virginia He., M.,d Rigoberto T., G., “Removal of Heavy Metals Using Adsorption Processes Subject to an External Magnetic Field”, http://dx.doi.org/10.5772/intechopen.74050,2018.