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Modelling the Effect of Nanoscale Zero-Valent Iron (nZVI), Biochar (BC) and Nanoscale Zero-Valent Iron/Biochar (nZVI/BC) on the Adsorption/Reduction of Nitrobenzene (NB)

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ABSTRACT

In most instances, there exists an inaccuracy in interpretation of adsorption/reduction of substances using linear technique as it can only provide an approximate value of the measured parameter; the specific adsorption rate. This paper provides for the first-time modelling of the effect of nZVI/BC, nZVI and Biochar (BC) on the adsorption/reduction of nitrobenzene as modelled using Pseudo-1st order (PFO), Pseudo-2nd Order (PSO), Elovich and Avrami models. Pseudo-1st Order was the best model for nZVIBCg, whereas Pseudo-2nd Order was the best model for nZVI and BC on Nitrobenzene (NB) removal based on statistical dependencies that were used such as root-mean-squire error (RMSE), bias factor (BF), Akaike information criterion (AICc) and the adjusted coefficient of determination. Justifiably from the results, coupling nZVI and BC together will help in reducing more of NB than when individual compounds are used.

INTRODUCTION

The use of zero-valent iron (ZVI) in the elimination of harmful pollutants in groundwater and wastewater has gained widespread interest in recent years [1–3]. ZVI materials have been lengthily applied in reducing of aqueous organic pollutants owing to the fact of its ability as a reducing agent together with – 0.43 V standard electrode potential to which it possesses. Example of such reducible pollutants include chlorohydrocarbon [4] and chlorinated phenols [5], anions [e.g., CrO42- [6], AsO43- [7] and SeO42- [8]] and heavy metals [e.g., Pb (II) [9] and Hg(II) [10]], as a result of large particular surface area, relative low price and remarkable surface reactivity [11].

The nanoscale zero valent iron (nZVI) displayed many benefits, including low dosage and high reactivity, relative to microscale ZVI, with decreasing particle size and correspondingly large specific surface area. This provides nZVI with great opportunities for contaminant remediation. However, given the strong magnetic force between particles and high surface energy, which restricts use, the major challenges associated with nZVI include strong agglomeration and rapid oxidation in air [12]. It is possible to classify the countermeasures into two major groups, i.e. surface decoration with surfactants and support delivery. Surfactants are used widely to relieve the accumulation of particles and improve properties of adsorption [13], thus, enhancing the reactivity of nZVI can improve the reactivity of nZVI. Nevertheless, the diffusion and desorption of surfactants into a liquid phase can lead to lesser pollution [14]. Stabilizing nanoparticles on aids, which may be more promising to increase stability, is another promising method. Not only does this routine increase the distribution of nZVI particles, but it also encourages activity by nZVI interaction and facilitates activity [15]. Consequently, many supports ranging from Fe_3O_4 and TiO_2 [16], clay minerals [17,18] and Zeolites [19] have been established for nZVI. Drawbacks, such as a complicated planning phase and the high cost of carrier materials, exist, however. The discovery of cheaper and more usable carrier materials is therefore demanding but important.

Biochar (BC) has recently attracted concern as a potential material for environmental remediation. BC is generated at low cost under oxygen-limited conditions from the pyrolysis of carbonaceous biomass or other solid waste [20]. BC can be applied to stabilize and spread engineered nanoparticles with its large specific surface area, rich porous composition, strong strength and abundant surface functional groups [21], which increases their mobility and durability, and decreases metal leachability. It is thus a promising medium of dispersion for nZVI. It was necessary to predict the flexible properties of BC assisting nZVI (nZVI/BC) in the purification of contaminants. In the one side, a mass of functional groups containing oxygen, e.g. carboxyl (-COOH) and hydroxyl (-OH), reinvest the great adsorption effects of BC against organic pollutants and heavy metals [22]. In the other hand, nZVI, by reduction after adsorption, is extremely active in the remediation of pollutants. In addition, BC will serve as an electron transfer mediator between nZVI and pollutants, which could speed up the reaction [23]. To date, nZVI/BC has acted as a sorbent for [24], Pb (II) [25] and tetracycline [26], a Cr (VI) reductant [27] and a trichloroethylene degradation persulfate activator [28]. However, the reducibility of nZVI/BC to organic contaminants has been less studied in comparison, particularly in terms of the synergistic effects between nZVI and BC and reaction state optimization, while trichloroethylene [29] and chloramphenicolol [30] have recently shown high removal efficiency.

The biochar, which was prepared by pyrolysis of oak sawdust, was assisted by nZVI in the original paper [31]. The anaerobic elimination of nitrobenzene has been tested for the adsorption and reduction properties of nZVI/BC (NB). In a variety of various manufacturing operations, including medicine, dyes, plastics, explosives and pesticides, NB is manufactured on a broad scale and commonly used as a raw material [32,33]. It has been shown to have high hydrophobicity, toxicity and persistence. At least 7 of the 1177 sites collected by the USEPA National Priorities List [34].

Conventional biological methods are unsuccessful in the treatment of NB-rich wastewaters, where the NB concentration is above 100 mg/L [35], as a result of the electro-withdrawing effect of the nitro group [36]. Advanced oxidation processes (AOPs) are therefore not sufficient for the removal of NB, considering the downside of the high cost and yield of the extremely toxic by-product of 1,3-dinitrobenzene [37]. Given the low cost, environmental benignity, and high reduction potential of nZVI, the reduction of nitro-aromatic by nZVI could be promising. In addition, the reduction of NB to aniline (AN) transition will decrease toxicity and increase biodegradability, encouraging subsequent biological treatment [38].

Mathematical modelling is the practice of translating problems from a field of application into tractable mathematical formulas whose theoretical and numerical analysis provides inspiration, solutions, and advice useful for the originating application [6]. A model is a framework for describing and evaluating a system's logical or mathematical representation. For the first time the predictive mathematical modeling of the effect of nZVI/BC effect on the adsorption of NB was studied by utilizing Pseudo-1st-Order, Pseudo-2nd-Order, Elovich and Avrami models (**Table 1**). The objectives in this paper is to find out the best model for both nZVI/BC, nZVI and BC on NB removal and to compare the reactivity of nZVI/BC on the adsorption of NB as against individual nZVI and BC.

MATERIALS AND METHODS

The Webplotdigitizer 2.5 [31]software was used to process the data gotten from fig 3 of [31]. Moreover, the reliability of the software which was utilized in scanning the figure has been approved and acknowledged by various researchers [39,40].

Statistical analysis

Many methods were used to distinguish between the models used. Such significant statistical difference was achieved by calculating the AICc (Akaike information criterion), bias factor (BF), adjusted coefficient of determination (R^2) and root mean-squire error (RMSE) among the methods of calculation used.

Fitting of the data

Pseudo-1st-Order, Pseudo-2nd-Order, Elovich and Avrami models were used in modelling and extracting fittings (see **Table 1**) of the adsorption graphical curves which was conducted with nonlinear regression using Curve-Expert Professional software (version 2.6.3). modelling was done by plotting Qt (maximum adsorption at given time) on the Y-axis and T (time) on the X-axis.

Table 1. Models used in this work.

Model	P	Equation
Pseudo-1st Order	2	$qt = qe[1 - \text{Exp}\,(-kl * t)]$
Pseudo-2nd Order	2	$qt = \dfrac{k2qe2t}{1 + qek2t}$
Elovich	2	$qt = \left[\dfrac{1}{bIn(ab)}\right] + \left[\dfrac{1}{bIn(x)}\right]$
Avrami	2	$qt = qe[1 - \text{Exp}(-kavt)\,n]$

Note:
qt = maximum adsorption at given time
qe = maximum adsorption capacity at equilibrium (experimental) should be computer calculated
Kl = Equilibrium constant of adsorption reaction
t = time

RESULTS AND DISCUSSION

The curves fittings in all the graphs presents acceptability (**Figs 2** to **13**). Before conducting modelling, the data were converted to log unit. Performance of Pseudo-2nd-order model on the effect of nZVIBC on the adsorption of NB was found to be the best as a result of its lowest RMSE, AICc values coupled with its high adjusted R^2 value. Moreover, values for BF and AF revealed the model's good acceptability having values close to 1.0. However, poorest performance was seen with Avrami model (**Table 2**). Additionally, the performance also of Pseudo-1st-order model on the effect of nZVI on the adsorption of NB was found to be the best due to its lowest RMSE, AICc values together with its high adjusted R^2 value. Values for BF and AF also shows the model's good acceptability having values close to 1.0. Lastly, it was found that Pseudo-2nd-order still has the best performance on the effect of BC on the adsorption of NB due to its lowest RMSE, AICc values and high adjusted R^2 value. Values for BF and AF also shows the model's good suitability having values close to 1.0.

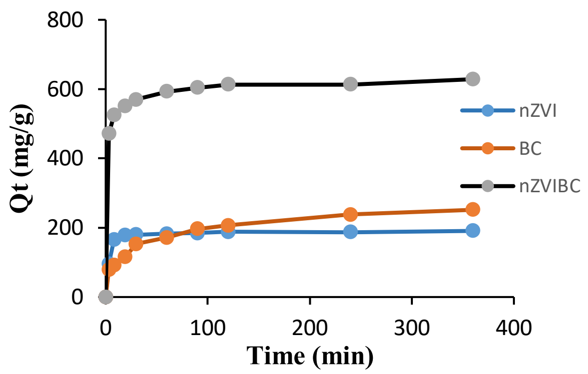

Fig. 1. Data replotted on the effect of nZVI, BC and nZVI/BC on the adsorption/reduction of NB.

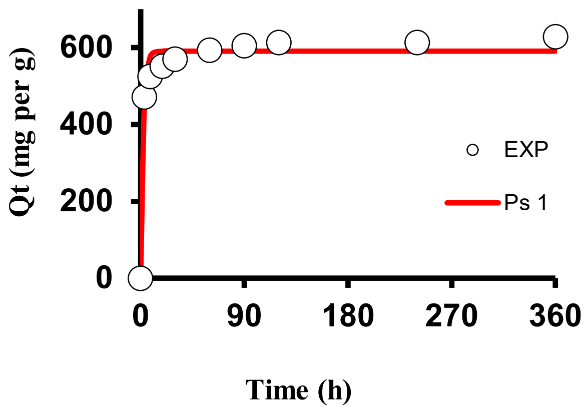

Fig 2. The effect of nZVI/BC on the adsorption of NB as modelled using the Pseudo-1st-order model.

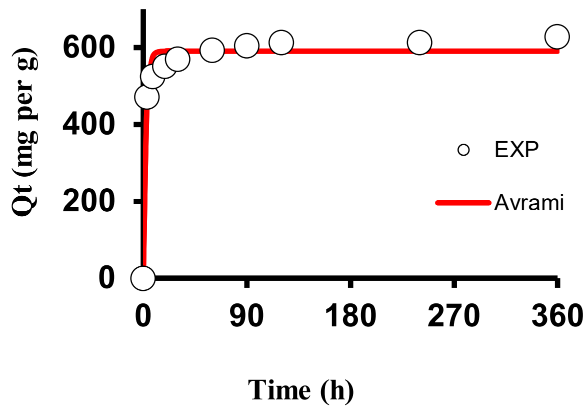

Fig 5. The effect of nZVI/BC on the adsorption of NB as modelled using the Avrami model.

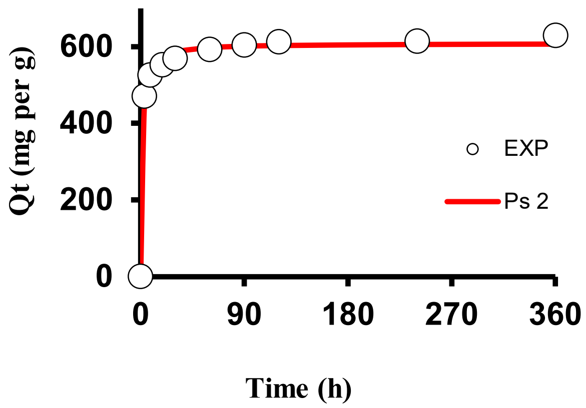

Fig 3. The effect of nZVI/BC on the adsorption of NB as modelled using the Pseudo-2st-order model.

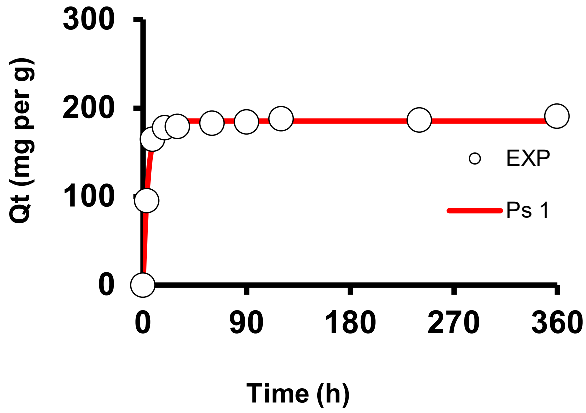

Fig 6. The effect of nZVI on the adsorption of NB as modelled using the Pseudo-1st-otder model.

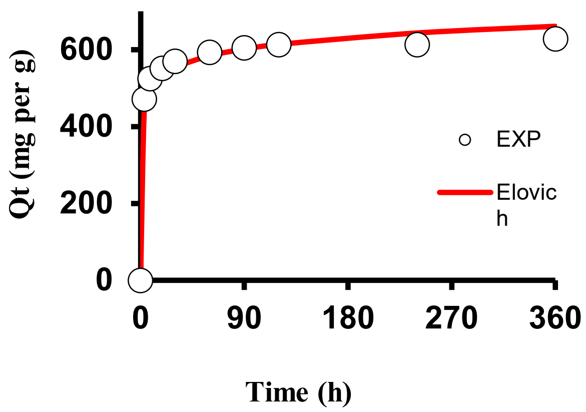

Fig 4. The effect of nZVI/BC on the adsorption of NB as modelled using the Elovich model.

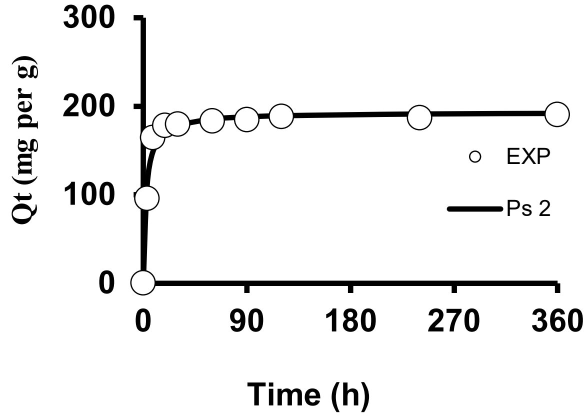

Fig 7. The effect of nZVI on the adsorption of NB as modelled using the Pseudo-2st-order model.

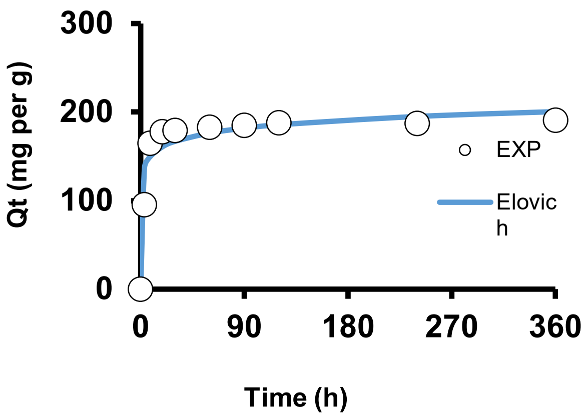

Fig 8. The effect of nZVI on the adsorption of NB as modelled using the Elovich model.

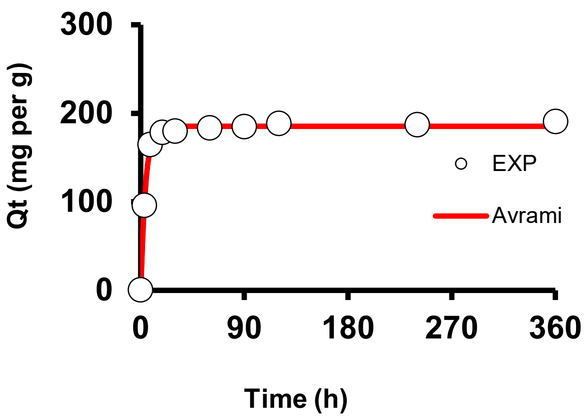

Fig 9. The effect of nZVI on the adsorption of NB as modelled using the Avrami model.

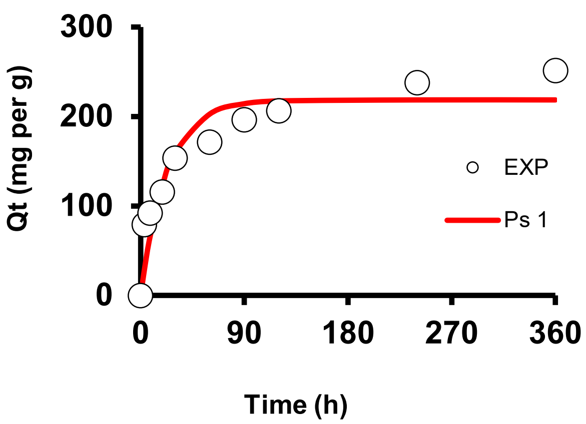

Fig 10. The effect of BC on the adsorption of NB as modelled using the Pseudo-1st-order model.

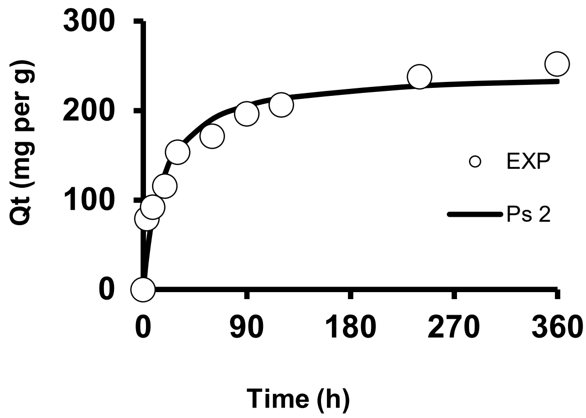

Fig 11. The effect of BC on the adsorption of NB as modelled using the Pseudo-2st-order model.

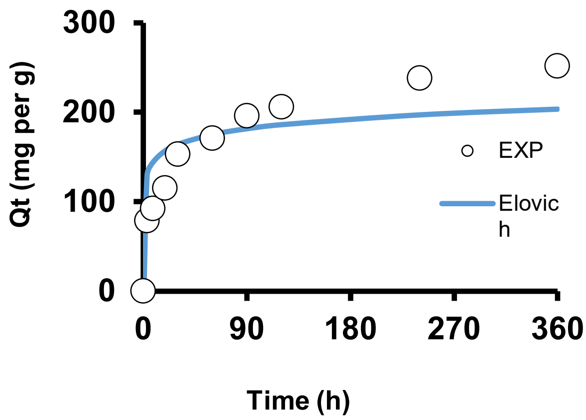

Fig 12. The effect of BC on the adsorption of NB as modelled using the Elovich model.

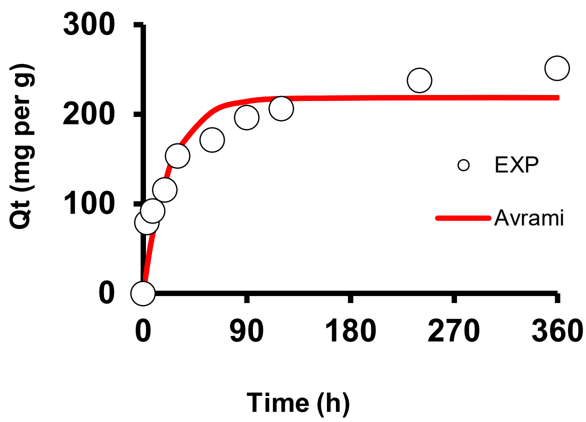

Fig 13. The effect of BC on the adsorption of NB as modelled using the Avrami model.

Table 2. Statistical analysis for the models used in modelling the effect of nZVIBC on the adsorption of NB

Model	p	RMSE	*Adr²*	AICc	AF	BF
Pseudo-1st Order	2	30.467	0.96943	80.10	1.040	1.000
Pseudo-2nd Order	2	15.283	0.992	66.30	1.021	1.000
Elovich	2	21.056	0.985	72.71	1.025	0.995
Avrami	2	30.467	0.969	80.10	80.101	0.995

Table 3. Statistical analysis for the models used in modelling the effect of nZVI on the adsorption of NB

Model	p	RMSE	*Adr²*	AICc	AF	BF
Pseudo-1st Order	2	4.468	0.99385	41.71	1.021	1.002
Pseudo-2nd Order	2	8.405	0.978	54.34	1.037	1.005
Elovich	2	18.187	0.891	69.78	1.082	1.012
Avrami	2	4.468	0.994	41.71	41.706	1.012

Table 4. Statistical analysis for the models used in modelling the effect of BC on the adsorption of NB

Model	p	RMSE	*Adr²*	AICc	AF	BF
Pseudo-1st Order	2	27.733	0.87913	78.22	1.216	0.893
Pseudo-2nd Order	2	18.785	0.941	70.43	1.134	0.940
Elovich	2	40.166	0.617	85.63	1.211	1.079
Avrami	2	27.733	0.879	78.22	78.221	1.079

Note:
P: no of parameters
adJR² Adjusted coefficient of determination
RMSE Root Mean Square Error
BF: Bias factor
AF: Accuracy factor

Based on the statistical analysis presented in this paper, the Pseudo-1st order turn out to be the best model for nanoscale zero-valent iron/Biochar, nZVI/BC effect on reduction/adsorption of nitrobenzene, NB. Similarly, it was seen separately that, the best model for the nanoscale zero-valent iron, nZVI and Biochar, BC effects on the reduction/adsorption of nitrobenzene is Pseudo-2nd order. Such statistical dependencies that were used include the root-mean-squire error (RMSE), bias factor (BF), Akaike information criterion (AICc) and the adjusted coefficient of determination. The results indicate reliability of nZVI and BC as potential candidates for the adsorption of nitrobenzene and other compounds as many researchers suggested. Moreover, it also revealed that BC can effectively enhance the adsorption capability of nZVI when coupled together and more of a substance would be adsorbed as compared to when these compounds are used individually

CONCLUSION

In conclusion therefore, Pseudo-1st-Order and Pseudo-2nd-Order were the best models for modelling the effect of nZVI/BC, nZVI and BC adsorption on NB. There is also a clear evidence toward the enhancement of both nZVI and BC on the removal of NB when coupled together i.e nZVI/BC. Further study on other secondary models will indeed be a breakthrough.

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REFERENCES

1. Gang X, Wang Q, Qian Y, Gao P, Su Y, Liu Z, et al. Simultaneous removal of aniline, antimony and chromium by ZVI coupled with H2O2: Implication for textile wastewater treatment. J Hazard Mater. 2019;368(October 2018):840–8.
2. Tian J, Jin J, Chiu PC, Cha DK, Guo M, Imhoff PT. A pilot-scale, bi-layer bioretention system with biochar and zero-valent iron for enhanced nitrate removal from stormwater. Water Res. 2019;148:378–87.
3. Wang M, Cheng W, Wan T, Hu B, Zhu Y, Song X, et al. Mechanistic investigation of U(VI) sequestration by zero-valent iron/activated carbon composites. Chem Eng J. 2019;362(December 2018):99–106.
4. Agegnehu G, Srivastava AK, Bird MI. The role of biochar and biochar-compost in improving soil quality and crop performance: A review. Appl Soil Ecol. 2017;119(October 2016):156–70.
5. Minella M, Sappa E, Hanna K, Barsotti F, Maurino V, Minero C, et al. Considerable Fenton and photo-Fenton reactivity of passivated zero-valent iron. RSC Adv. 2016;6(89):86752–61.
6. Yuan Y, Chen H, Yuan W, Williams D, Walker JT, Shi W. Is biochar-manure co-compost a better solution for soil health improvement and N2O emissions mitigation? Soil Biol Biochem. 2017;113:14–25.
7. Ouyang W, Huang W, Hao X, Tysklind M, Haglund P, Hao F. Watershed soil Cd loss after long-term agricultural practice and biochar amendment under four rainfall levels. Water Res. 2017;122:692–700.
8. Feng Y, Lu H, Liu Y, Xue L, Dionysiou DD, Yang L, et al. Nano-cerium oxide functionalized biochar for phosphate retention: preparation, optimization and rice paddy application. Chemosphere. 2017;185(50):816–25.
9. Khan W ud D, Ramzani PMA, Anjum S, Abbas F, Iqbal M, Yasar A, et al. Potential of miscanthus biochar to improve sandy soil health, in situ nickel immobilization in soil and nutritional quality of spinach. Chemosphere. 2017;185:1144–56.
10. Lin Y, Ding W, Liu D, He T, Yoo G, Yuan J, et al. Wheat straw-derived biochar amendment stimulated N2O emissions from rice paddy soils by regulating the amoA genes of ammonia-oxidizing bacteria. Soil Biol Biochem. 2017;113:89–98.
11. Li J, Dou X, Qin H, Sun Y, Yin D, Guan X. Characterization methods of zerovalent iron for water treatment and remediation. Water Res. 2019;148:70–85.
12. Tan Z, Liu L, Zhang L, Huang Q. Mechanistic study of the influence of pyrolysis conditions on potassium speciation in biochar "preparation-application" process. Sci Total Environ. 2017;599–600:207–16.
13. Zheng Z, Lu G, Wang R, Huang K, Tao X, Yang Y, et al. Effects of surfactant on the degradation of 2,2″,4,4″-tetrabromodiphenyl ether (BDE-47) by nanoscale Ag/Fe particles: Kinetics, mechanisms and intermediates. Environ Pollut. 2019;245:780–8.
14. Brassard P, Godbout S, Raghavan V. Pyrolysis in auger reactors for biochar and bio-oil production: A review. Biosyst Eng. 2017;161:80–92.
15. Crampon M, Hellal J, Mouvet C, Wille G, Michel C, Wiener A, et al. Do natural biofilm impact nZVI mobility and interactions with porous media? A column study. Sci Total Environ. 2018;610–611:709–19.
16. Tan L, Lu S, Fang Z, Cheng W, Tsang EP. Enhanced reductive debromination and subsequent oxidative ring-opening of decabromodiphenyl ether by integrated catalyst of nZVI supported on magnetic Fe3O4 nanoparticles. Appl Catal B Environ. 2017;200:200–10.
17. Yuan P, Fan M, Yang D, He H, Liu D, Yuan A, et al. Montmorillonite-supported magnetite nanoparticles for the removal of hexavalent chromium [Cr(VI)] from aqueous solutions. J Hazard Mater. 2009;166(2–3):821–9.

18. Ezzatahmadi N, Ayoko GA, Millar GJ, Speight R, Yan C, Li J, et al. Clay-supported nanoscale zero-valent iron composite materials for the remediation of contaminated aqueous solutions: A review. Chem Eng J. 2017;312:336–50.
19. Arancibia-Miranda N, Baltazar SE, García A, Muñoz-Lira D, Sepúlveda P, Rubio MA, et al. Nanoscale zero valent supported by Zeolite and Montmorillonite: Template effect of the removal of lead ion from an aqueous solution. J Hazard Mater. 2016;301:371–80.
20. Chen B, Chen Z, Lv S. A novel magnetic biochar efficiently sorbs organic pollutants and phosphate. Bioresour Technol. 2011;102(2):716–23.
21. Devi P, Saroha AK. Simultaneous adsorption and dechlorination of pentachlorophenol from effluent by Ni-ZVI magnetic biochar composites synthesized from paper mill sludge. Chem Eng J. 2015;271:195–203.
22. Chun Y, Sheng G, Chiou GT, Xing B. Compositions and sorptive properties of crop residue-derived chars. Environ Sci Technol. 2004;38(17):4649–55.
23. Oh SY, Son JG, Chiu PC. Biochar-mediated reductive transformation of nitro herbicides and explosives. Environ Toxicol Chem. 2013;32(3):501–8.
24. Chi T, Zuo J, Liu F. Performance and mechanism for cadmium and lead adsorption from water and soil by corn straw biochar. Front Environ Sci Eng. 2017;11(2).
25. Rama Chandraiah M. Facile synthesis of zero valent iron magnetic biochar composites for Pb(II) removal from the aqueous medium. Alex Eng J. 2016;55(1):619–25.
26. Wang X, Lian W, Sun X, Ma J, Ning P. Immobilization of NZVI in polydopamine surface-modified biochar for adsorption and degradation of tetracycline in aqueous solution. Front Environ Sci Eng. 2018;12(4).
27. Dong H, Deng J, Xie Y, Zhang C, Jiang Z, Cheng Y, et al. Stabilization of nanoscale zero-valent iron (nZVI) with modified biochar for Cr(VI) removal from aqueous solution. J Hazard Mater. 2017;332:79–86.
28. Yan J, Han L, Gao W, Xue S, Chen M. Biochar supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. Bioresour Technol. 2015;175:269–74.
29. Dong H, Zhang C, Hou K, Cheng Y, Deng J, Jiang Z, et al. Removal of trichloroethylene by biochar supported nanoscale zero-valent iron in aqueous solution. Sep Purif Technol. 2017;188:188–96.
30. Ahmed MB, Zhou JL, Ngo HH, Guo W, Johir MAH, Sornalingam K, et al. Nano-Fe0 immobilized onto functionalized biochar gaining excellent stability during sorption and reduction of chloramphenicol via transforming to reusable magnetic composite. Chem Eng J. 2017;322:571–81.
31. Wei G, Zhang J, Luo J, Xue H, Huang D, Cheng Z, et al. Nanoscale zero-valent iron supported on biochar for the highly efficient removal of nitrobenzene. Front Environ Sci Eng. 2019;13(4).
32. Huang J, Wen Y, Ding N, Xu Y, Zhou Q. Effect of sulfate on anaerobic reduction of nitrobenzene with acetate or propionate as an electron donor. Water Res. 2012;46(14):4361–70.
33. Zhao Y, Lin L, Hong M. Nitrobenzene contamination of groundwater in a petrochemical industry site. Front Environ Sci Eng. 2019;13(2).
34. Cai Z, Fu J, Du P, Zhao X, Hao X, Liu W, et al. Reduction of nitrobenzene in aqueous and soil phases using carboxymethyl cellulose stabilized zero-valent iron nanoparticles. Chem Eng J. 2018;332(September 2017):227–36.
35. Hu X, Li A, Fan J, Deng C, Zhang Q. Biotreatment of p-nitrophenol and nitrobenzene in mixed wastewater through selective bioaugmentation. Bioresour Technol. 2008;99(10):4529–33.
36. Yin W, Wu J, Huang W, Wei C. Enhanced nitrobenzene removal and column longevity by coupled abiotic and biotic processes in zero-valent iron column. Chem Eng J. 2015;259:417–23.
37. Jiang BC, Lu ZY, Liu FQ, Li AM, Dai JJ, Xu L, et al. Inhibiting 1,3-dinitrobenzene formation in Fenton oxidation of nitrobenzene through a controllable reductive pretreatment with zero-valent iron. Chem Eng J. 2011;174(1):258–65.
38. Oh SY, Seo YD, Ryu KS. Reductive removal of 2,4-dinitrotoluene and 2,4-dichlorophenol with zero-valent iron-included biochar. Bioresour Technol. 2016;216:1014–21.
39. Halmi MIE, Shukor MS, Johari WLW, Shukor MY. Modeling the growth curves of *Acinetobacter* sp. strain DRY12 grown on diesel. J Environ Bioremediation Toxicol. 2014;2(1):33–7.
40. Khare KS, Phelan FR. Quantitative Comparison of Atomistic Simulations with Experiment for a Cross-Linked Epoxy: A Specific Volume-Cooling Rate Analysis. Macromolecules. 2018;51(2):564–75.