

## USING N-OVEL COATED SAND AS REACTIVE BED IN PERMEABLE BARRIER FOR ELIMINATION OF METHYL ORANGE DYE FROM GROUNDWATER\*

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### ABSTRACT

This study investigates the efficacy of sand coated with calcium / aluminum (Ca/Al)-layered double hydroxide (LDH) in the elimination of methyl orange dye from simulated groundwater using method of permeable reactive barrier. For green (sustainable) manufacturing of this sand, aluminum prepared from dissolution of alum (cheap coagulant) can be interacted chemically with calcium extracted from cement kiln dust byproduct to create nanoparticles of Ca and Al that precipitate on the filter sand. Sorption measurements for interaction of methyl orange dye and coated sand was well formulated by Langmuir model with highest value of correlation (determination coefficient= 0.999) and lowest errors (sum of squared errors= 0.0122). Also, the maximum capacity of adsorption was valued of 0.9453 mg/g and the sorption curve can classify as “favorable” type. According to desorption measurements, little percentage of dye (0.91%) can desorb from exhausted coated sand through washing with water due to strength of bonding between sorbent and dye molecules. Also, the exhausted sorbent can regenerate with efficiency not less than 85% after eight of regeneration cycles. Finally, measurements of breakthrough curves in the continuous mode operation using column setup proved that the propagation of dye front (and consequently the longevity of barrier) would increase significantly with thicker barrier and lowest values of influent concentration and flow rate. COMSOL (computer solution) package can use effectively in the simulation of these curves.

**Key words:** solute transport; methyl orange dye; alum; nanoparticles; cement kiln dust; permeable reactive barrier.

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شهاب و فيصل

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إستعمال رمل مطلي مبتكر كقاعدة تفاعلية في حاجز نفاذ لإزالة صبغة الميثيل البرتقالية من المياه الجوفية

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باحث

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تتحرى هذه الدراسة فعالية الرمل المطلي بطبقة مزدوجة من هيدروكسيد (LDH) الكالسيوم/الألومنيوم (Ca/Al) في إزالة صبغة الميثيل البرتقالية من مياه جوفية مصنعة باستخدام طريقة الحاجز التفاعلي النفاذ. تصنيع هذا الرمل بشكل أخضر (مستدام)، من تفاعل الألومنيوم المحضر من إذابة الشب (مادة تخثر رخيصة) كيميائياً مع الكالسيوم المستخلص من المنتج الثانوي لغبار فرن الأسمت لتكوين جزيئات نانوية من الكالسيوم والألومنيوم تترسب على الرمل المرشح. تمت صياغة قياسات الامتصاص لتفاعل صبغة الميثيل البرتقالية والرمل المطلي بشكل جيد بواسطة نموذج Langmuir مع أعلى قيمة للارتباط (معامل التحديد = 0.999) وأدنى خطأ (مجموع الأخطاء التربيعية = 0.0122). أيضاً ، قدرت السعة القصوى للامتصاص بـ 0.9453 ملغم/ غرام ويمكن تصنيف منحنى الامتصاص على إنه نوع "مفضل". وفقاً لقياسات الإزالة ، يمكن إزالة نسبة قليلة من الصبغة (0.91%) من الرمال المطلية المستنفذة من خلال الغسل بالماء بسبب قوة الترابط بين جزيئات المادة الماصة والصبغة. أيضاً ، يمكن أن تتجدد المادة الماصة المستنفذة بكفاءة لا تقل عن 85% بعد ثماني دورات تجديد. أخيراً ، أثبتت قياسات منحنيات الاختراق في عملية الوضع المستمر باستخدام نظام العمود أن انتشار جبهة الصبغة (وبالتالي طول عمر الحاجز) سيزداد بشكل كبير مع وجود حاجز أكثر سمكاً وأدنى قيم للتركيز المؤثر ومعدل التدفق. يمكن استخدام حزمة COMSOL (حل الكمبيوتر) بشكل فعال في محاكاة هذه المنحنيات .

الكلمات المفتاحية: نقل المذاب؛ صبغة الميثيل البرتقالية؛ الشب؛ الجسيمات النانوية؛ غبار فرن الأسمت؛ حاجز تفاعلي نفاذ.

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## INTRODUCTION

The contamination of surface and subsurface water resources with different types of chemicals especially the dyes are an undeniable issue (5). The textile industry is the prime source for pollution of water bodies especially the records of “World Bank” proved that 20% of global water contamination results from the textiles dyeing and treatment. The dyeing steps require to utilize different reagents which are rich with chemical compounds; so, these industrial processes can consider unfriendly for environment (25). Dyes in water can absorb light, decrease the water transparency, consume the oxygen dissolved in water, cause hypoxia in water body, affect the growth of aquatic organisms, damage the self-purification, and cause visual contamination (2, 3, 30). Methyl orange is a mutagenic dye which has slight water solubility. At  $\text{pH} > 4.4$ , its color is yellow and it changes to red at  $\text{pH} < 4.4$ ; hence, this dye can use as an indicator. Methyl orange is also utilized extensively in textile industry. It forms type of azo dyes that have high resistance to biodegradability. Thus, this dye is utilized as a model for investigation the cleanup of environment (31). The continuous up-to-date for methods of remediation must be conducted to control of this contamination. The traditional technique used historically for restoration of groundwater is “pump and treat”; unfortunately, many studies proved that the efficacy of this technique can decrease drastically in the long period time. This method requires the pumping of groundwater to the surface of ground to treat it by popular methods like ion exchange, flotation, adsorption, and others. Then, treated water can re-inject to the subsurface system, blending with surface water or can dispose to sewer system. An alternatively for this method, permeable reactive barrier (PRB) was developed as promising technique for reclamation of groundwater. The PRB depends on the construction of trench perpendicular on the groundwater pathway which must be filled with reactive material to pass of water and trapping of contaminant(4). The choosing the proper substance for PRB is the critical step because it must have two important characteristic specifically acceptable

permeability and high reactivity. Also, this substance should be compatible with ambient aquifer, not lead to byproducts when interact with plume of chemicals, and not will be source for chemical itself (23). Various reactive materials like activated carbon, magnetic porous polymers, natural biosorbent, and nanofibrous sorbents have been used to remove of dyes (25, 26, 27, 29). Previous studies certified that there are many drawbacks (related with cost and capacity of sorption) in the application of these sorbents in the treatment of water contained dyes. Thus, the production of more effective sorbents with high durability and acceptable cost is the aim of recent studies. In this direction, the synthesis of Layered Double Hydroxides (LDHs) was taken appreciable attention especially in the field of environment. The synthesis process is simple and inexpensive in the laboratory and industrial scales. The LDHs are attractive as reactive medium for a wide number of anions (15), cations (19), radionuclides (6), and dyes (3). LDHs can remove wide range of chemicals through exchange with inter-layer anions as proved by many researches. Mg/Fe and Ni/Fe LDHs, with molar ratio ( $\text{M}^{2+}/\text{Fe}^{3+}$ ) = 3 and synthesized by co-precipitation, was utilized to remove of malachite green, methyl orange, and methylene blue from wastewater. Pseudo-second order is well described the sorption data and thermodynamic analysis signified that sorption of this dye was spontaneous, exothermic for anionic dye and endothermic for cationic ones (10). This work aims to produce of novel sorbent named “sand coated with (Ca/Al)-LDH” from precipitation of aluminum and calcium onto filter sand. This sorbent was tested to evaluate its capability in the treatment of simulated wastewater contained of methyl orange dye.

## MATERIALS AND METHODS

**Contaminant:** This work was chosen the methyl orange dye (supplied from HIMEDIA company – India) to contaminate the water. At room temperature, specific mass of this dye was thoroughly mixed with 1 L distilled water to get stock solution contaminated with 1000 mg/L initial concentration ( $C_0$ ) of methyl orange dye; however, water samples with certain concentration can obtain by diluting of

this solution. The acidity of samples can modify by addition drops of 1 M hydrochloric acid or sodium hydroxide.

#### Sorbent

Filter sand, used extensively in the water supply unit, was chosen as solid matrix. This sand must to wash and sieve it where particles sizes ranged from 0.6 to 1 mm were selected. The porosity of sand was 0.45 while its specific gravity of 1.363. The filter sand is low reactive towards the contaminants; so, the convert it to reactive material can be investigated. Nanoparticles of calcium-extracted from Cement Kiln Dust (CKD)-and aluminum (from alum) are precipitated together on the surface of filter sand to generate new functional groups and binding sites by adopting the same procedure of manufacturing mentioned in previous work (12). The CKD supplied from Kirkuk Cement Factory and its specific gravity was equal to 2.77 as measured by American Society for Testing and Materials (ASTM C188-95).

#### Batch tests

Two sets of batch tests must be conducted as follows:

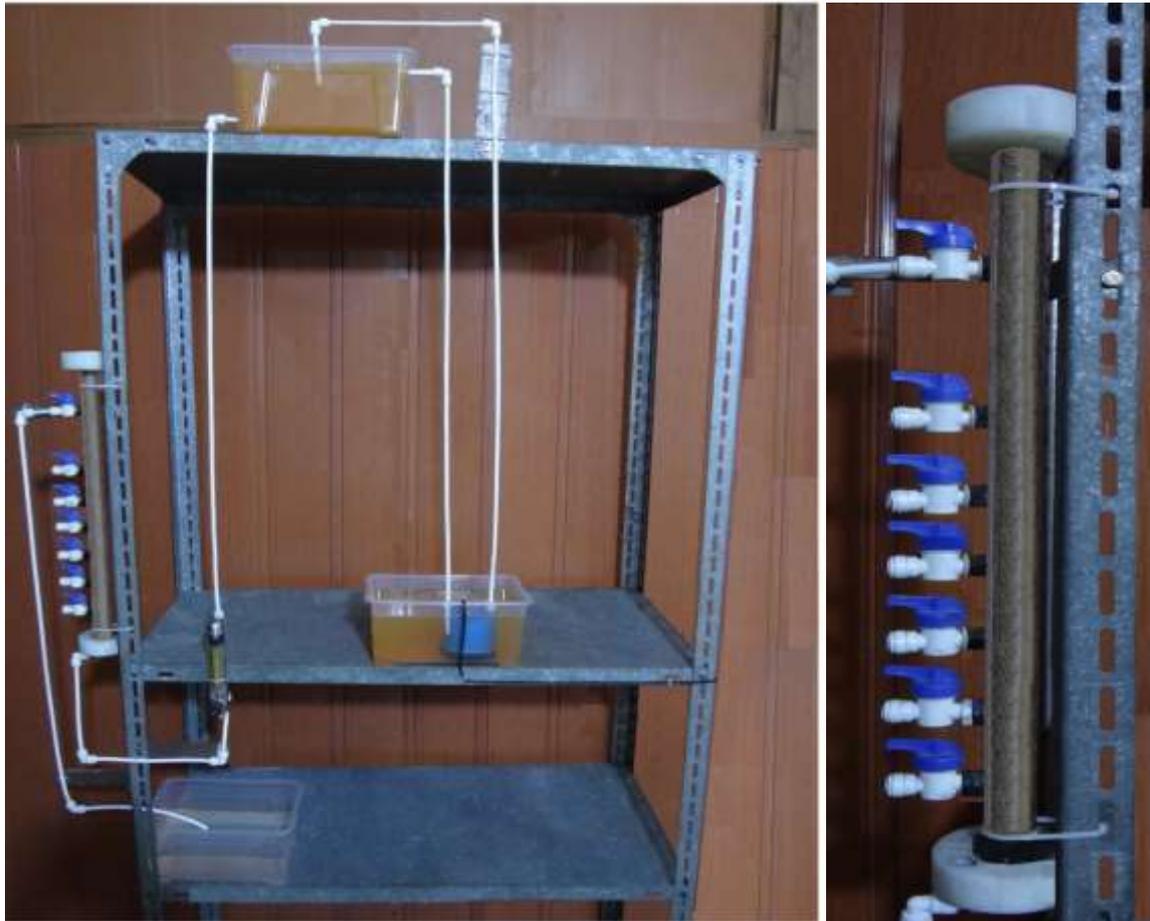
The first set is required to manufacture of “sand coated with (Ca/Al)-LDH”. The manufacturing process requires to extract of calcium from 1 g CKD dissolved in 100 mL with presence of 1.5 mL HCl. This calcium is added to aluminum produced from dissolution of alum with molar ratio of 2 and the solution must be precipitated on the 1 g/ 100 mL sand. However, more details about the preparation procedure and operation conditions are mentioned in the previous study of the present authors (12). The second set is required to find the best isotherm for sorption measurements due to interaction of methyl orange dye-aqueous solution with coated sand. The specified model for sorption isotherm is utilized to find the term of reaction in the solute migration along the packed bed. These

tests have conducted in set of 250 mL flasks and 50 mL of solution ( $V$ ) contained of 50 mg/L  $C_o$  of dye at initial pH 5 was distributed to each flask. Then, 0.4 g of the coated sand ( $m$ ) should be added; however, flasks must agitate at 200 rpm for 2 h and concentration at equilibrium state ( $C_e$ ) must determine UV spectrophotometer (Model UV T80, England). The sorbed dye on the solid particles ( $q_e$ ) calculates as follows:

$$q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

#### Continuous tests

The one Perspex column, with  $\phi=2.5$  cm and depth of 50 cm, is supplied with tubes, valves, flow meter, pump, constant head tank and storage tank to represent the experimental set-up for investigating the transport of water contaminated with methyl orange dye in one dimension as shown in Figure 1. The column was filled with coated sand to evaluate its performance in the elimination of adopted dye from stream of contaminated water. At room temperature, the packed bed must be fed with distilled water in the upward direction from the bottom of column to ensure that all voids filled with water (i.e. reach to saturated state). Then, the wastewater, contained of dye, was pumped to the packed sorbent by application of 5, 10, or 15 mL/min at specific hydraulic gradient. Discharges of flow must be enough low to ensure that the Reynold's number  $< 1-10$  for flow within packed bed (9). The column is equipped with six ports designated as P1 (5 cm), P2 (10 cm), P3 (15 cm), P4 (20 cm), P5 (25 cm) and P6 (30 cm). The monitoring of dye concentrations along the adopted column can achieve periodically by withdrawing water samples from mentioned ports. Also, the coefficient of permeability of the coated sand can calculate by Darcy's law after measuring the accumulative volumes of effluent and hydraulic gradient.



**Figure 1. Components and configuration of experimental set-up**

**Models of sorption isotherms and breakthrough curves:** The sorption data measured previously must be formulated mathematically to describe the relationship related between quantity of chemical sorbed onto coated sand ( $q_e$ ) and  $C_e$ . Popular expressions utilized frequently to represent this relationship are named “Freundlich” and “Langmuir” models; however, more information can be inserted below (1, 13, 15, 16, 17) :

1- Freundlich's model: has the following nonlinear formula:

$$q_e = K_f C_e^{1/n} \quad (2)$$

where  $K_f$  and  $n$  are Freundlich constants.

2- Langmuir model: had been derived by Irving Langmuir in 1916 and its nonlinear form can be written as follows:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \quad (3)$$

where  $q_m$  is the maximum adsorption capacity while  $b$  is the affinity between chemical and sorbent.

The relationship plotted the variation between normalized concentration ( $C/C_o$ ) and residence time in the column setup described previously

is known as “Advection-dispersion-reaction” or “solute transport” equation. This equation (Eq.4) is partial differential of first order with travel time ( $t$ ) and second order with distance ( $z$ ). For right hand side of this equation, the first term is referred to transport of chemical due to turbulent mixing and varied pathway (i.e. dispersion), the second term can represent the migration of chemical by pore water velocity (i.e. advection), and the last term from same side can represent of reaction occurred through chemical migration (i.e. sorption). This term can represent by isotherm model that must be incorporated with Eq.4 to find the spatial and temporal propagation of chemical front. However, the 1-D form of this equation will be as follows (13) :

$$D_z \frac{\partial^2 C}{\partial z^2} - V_z \frac{\partial C}{\partial z} \pm \frac{r}{n} = \frac{\partial C}{\partial t} \quad (4)$$

where  $C$  is the chemical concentration (mg/L),  $D_z$  is the coefficient of dispersion ( $\text{cm}^2/\text{s}$ ),  $V_z$  is the seepage velocity (cm/s), and  $n$  is the bed porosity. Eq.4 can solve by finite element numerical method using COMSOL multiphysics 3.5a (2008) software.

**RESULTS AND DISCUSSION**

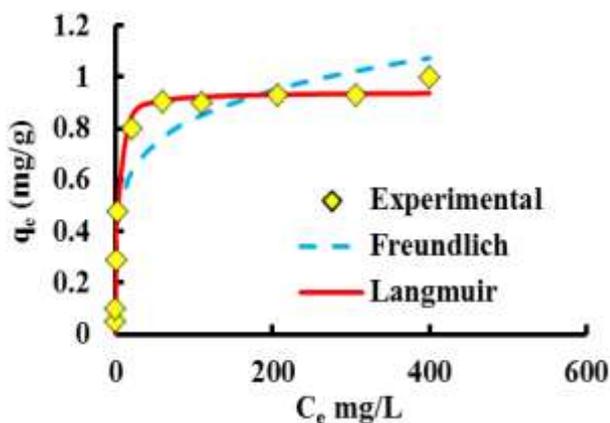
**Sorption isotherms:** The sorption measurements of methyl orange onto coated

sand are fitted with nonlinear forms of sorption models and their constants have been listed in Table 1 (10, 21).

**Table 1. Constants of models for sorption of methyl orange dye onto coated sand**

Model	Parameter	Value
Freundlich	$K_F$ (mg/g)(L/mg) <sup>1/n</sup>	0.350
	n	5.238
	R <sup>2</sup>	0.980
	SSE	0.0763
	q <sub>max</sub> (mg/g)	0.9453
	b (L/mg)	0.421
Langmuir	R <sup>2</sup>	0.999
	SSE	0.0122

This table certifies that the Langmuir can formulate sorption data with more acceptable manner in comparison with Freundlich relationship where determination coefficient (R<sup>2</sup>) =0.999 and sum of squared errors (SSE)= 0.0122; however, the concurrence between measurements and predications of isotherm models can illustrate in Figure 2. Separation parameter is equal to  $\frac{1}{1+bC_o}$  and it's values were ranged from 0 to 1 which means that the sorption curves classify as favorable (24) . Table 1 signified that the value of highest adsorption capacity for interaction of coated sand and methyl orange dye is 0.945 mg/g while affinity constant of 0.421 L/mg. The Freundlich constants K<sub>F</sub> and n were valued to be 0.35 (mg/g) (L/mg)<sup>1/n</sup> and 5.238 respectively.



**Figure 2. Sorption isotherms simulated the interaction of methyl orange-coated sand**

**Desorption kinetics**  
The effectiveness and potential of sorbent can evaluate by the desorption characteristics. At pH=7 and speed=200 rpm, the coated sand was used in the elimination of methyl orange dye with C<sub>o</sub> of 50 mg/L from wastewater and the final concentrations have been recorded for

duration of 2880 min as in Figure 3. It is obvious that final concentration will be remained around 2.564 mg/L after 30 min to obtain the efficiency of 94.8%. It is important to calculate the percentage of methyl orange dye that can desorb from exhausted coated sand through washing it by deionized water; however, results of desorption experiment can be observed in Figure 3. The analysis for final dye concentration proved that just 0.91% of dye can be liberated from exhausted sorbent for same duration of sorption process (i.e. 2880 min)(8) . The strong bonding between the adopted dye and coated sand may be the reason for this low desorption percent; so, this sand can classify as dependable sorbent for removal of days.

**Recyclability**

Tests included of adsorption–desorption cycles to access the regeneration of coated sand loaded with methyl orange dye must be applied. The aqueous solution of 0.5 M HCl can be utilized for washing of exhausted sorbent during the process of regeneration to desorb the adopted dye. The regeneration efficiencies (or percentages of dyeremoval) for coated sand are determined for each recycle run as illustrated in Figure 4 under conditions of pH=7, C<sub>o</sub>=50 mg/L, contact time=1 (equilibrium time is 1 h from batch experiment figure is not shown here), speed=200 rpm and dosage=5 g/50 mL. For eight cycles, specific reduction in the removal efficiencies can recognize for each recycle with maintaining on the percentage above 85%; however, the efficiencies are exceeded 94% after 4 cycles. The results documented that the coated sand can be effectively reusable and it is suitable candidate for sorption of present dye in the field applications (7) .

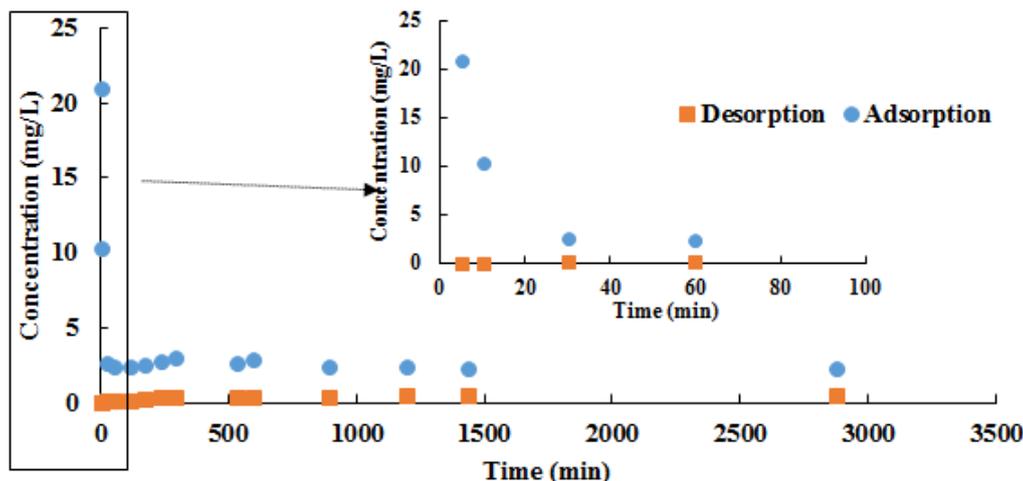


Figure 3. Desorption kinetics of methyl orange dye onto coated sand ( $C_o = 50$  mg/L; dosage= 0.2 g; contact time =48 hrs; initial pH =7; speed=200 rpm; desorption reagent: deionized water).  
 $C_o = 50$  mg/L; speed=200 rpm; time=1 h; dosage=5 g/50 mL, pH=7

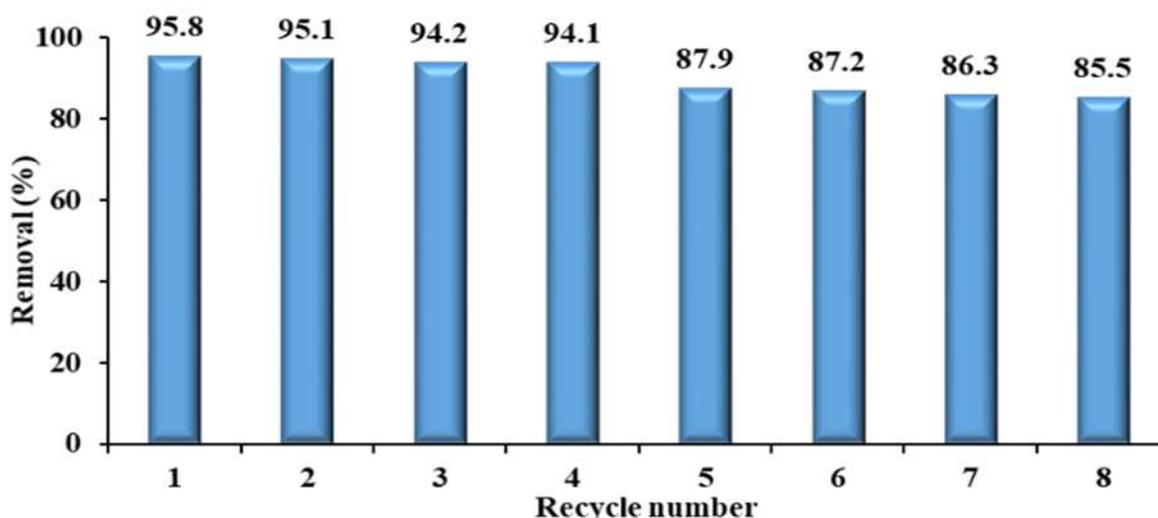


Figure 4. Efficiencies for removal of methyl orange from wastewater onto coated sand in the regeneration tests

**Propagation of methyl orange along coated sand:** The experimental procedure mentioned in the previous study (29) was applied to find the value of longitudinal dispersivity ( $\alpha_L$ ) for coated sand used as reactive material in the column. The solution of Eq. 4 requires to determine  $D_z$  of coated sand and this can calculate from  $\alpha_L$  multiplying by pore velocity plus the molecular diffusion coefficient. This solution represents the variation of normalized concentration ( $C/C_o$ ) along the bed of present sorbent for different values of time. Column filling with virgin sand was the first continuous test applied in this study for time=140 h to find the sand reactivity in the removal of considered dye where discharge of flow 5 mL/min and influent concentration of

50 mg/L port P6. Measurements of  $C/C_o$  at P6 demonstrated that the dye concentrations in the effluent water were varied around 47.2 mg/L during the test period and this proves the low reactivity of virgin sand. Breakthrough curves along column tests packed with “sand coated with (Ca/Al)-LDH” are measured and plotted in Figure 5 under different values of bed depths (from P1 to P6), flow rates and inlet dye concentration. For certain flow rate (i.e. 5 mL/min), Figure 5 proves that the increase of inlet concentrations through the range from 50 to 150 mg/L at fixed port will be associated with an obvious increase in the steepness of these curves; so, coated sand would be saturated with methyl orange in shorter time (21). Accordingly, the breakthrough and saturation points are corresponded to 5 and

90% of  $C/C_o$  respectively for adopted bed and dye can appear quickly with high inlet concentrations. Figure 5 reported that the breakthrough time at P6 was 10 h for 50 mg/L influent concentration and 5 mL/min flow rate, this time can reduce to 5 and 3.84 h for 100 and 150 mg/L respectively; however, the variation takes same trend for other ports. Figure 6 plots the breakthrough curves under the influence of water flow rate at all ports for 50 mg/L influent concentration. It seems that the change of flow from 5 mL/min (Figure

4(a)) to 10 and 15 mL/min (Figure 6) would enhance the appearance of dye front in shorter period; so, significant increase in the curves steepness can be observed because the dye leaves of packed bed before reaching to equilibrium (19). This means that the effluent dye concentration is increased drastically causing the decrease in the time of breakthrough. For instance, the change of flow from 5 to 15 mL/min for 50 mg/L at P6 can associate with evidence reduction in the time of breakthrough from 10 to 3 h.

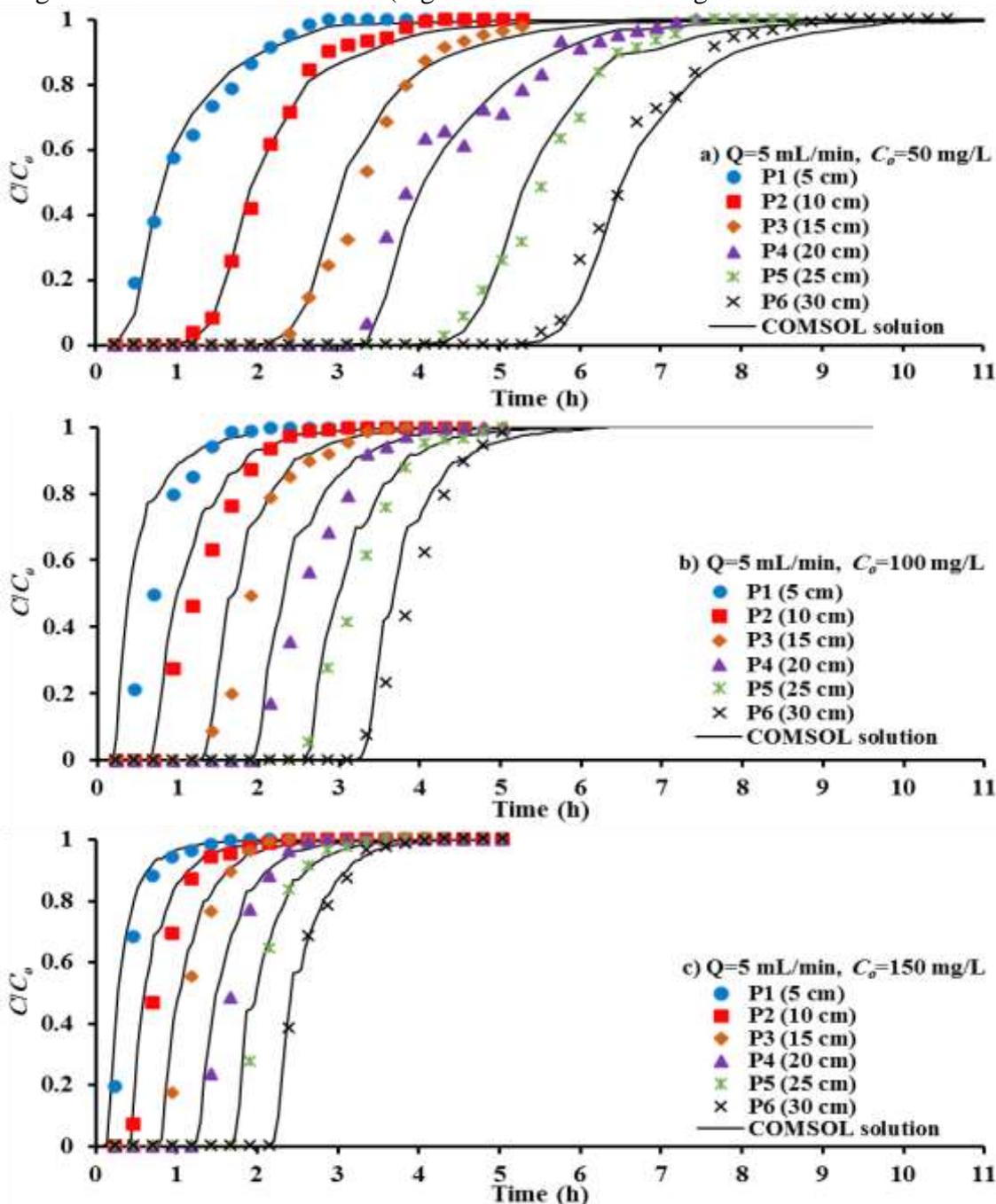
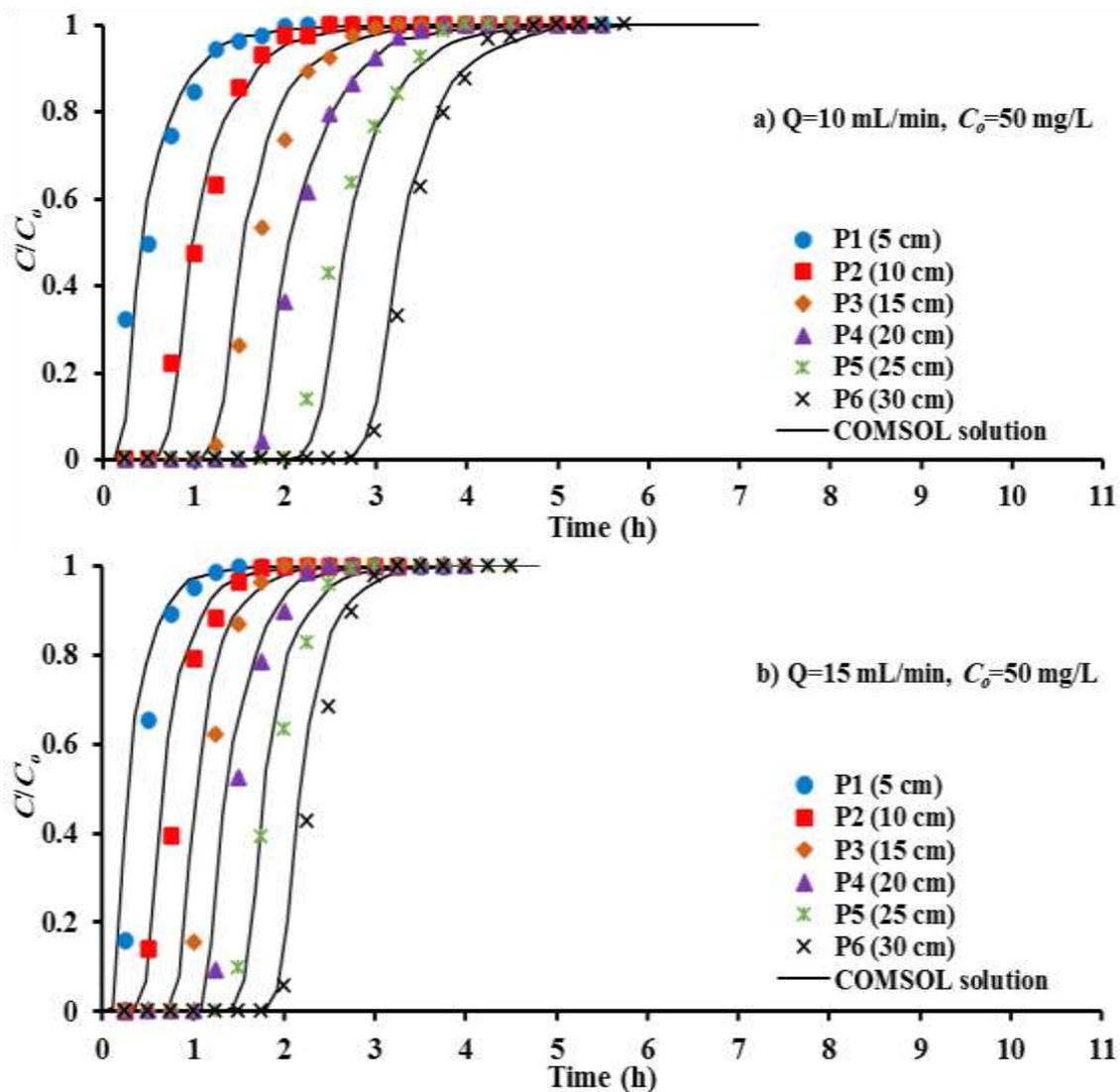


Figure 5. Measured breakthrough curves in comparison with COMSOL outputs for migration of water contained methyl orange dye along coated sand for various inlet concentrations



**Figure 6. Measured breakthrough curves in comparison with COMSOL outputs for migration of water contained methyl orange dye along coated sand for various flow rates**

Figures 5 and 6 certifies that the higher coated sand quantity can influence positively on the longevity of the barrier due to exist a clear delay in the appearance of dye front. So, the higher mass of coated sand in the column will give a good opportunity for dye molecules to sorb on the surfaces of solid particles and within their pores. The breakthrough time at P1 (5 cm) is 3 h for conditions of 5 mL/min and 50 mg/L; however, this time can increase to 10 h for P6 (30 cm). The solute transport equation was solved numerically as described previously using COMSOL package to simulate the continuous experimental tests. The outputs of this solution are plotted together with measurements of breakthrough curves as evidence in Figures 5 and 5 for mentioned depths under values of inlet concentrations and flow rates. Bulk density of  $1.371 \text{ g/cm}^3$ , dispersivity of 6.49 cm and

porosity of 0.43 are input constants applied for numerical solution. This solution was implemented with zero concentration initial condition while other conditions have been taken fixed concentration at bottom boundary and advective flux at upper side. An obvious matching between outputs of solution and measurements with  $R^2 > 0.98$  can recognize. The values of permeability coefficient were approximately stabilized at  $4.3 \times 10^{-1} \text{ cm/s}$  during the applied tests. The stabilization means that there is no blockage occurred in the pathways of moving water.

### Conclusions

Reaction of calcium extracted from CKD byproduct and aluminum produced from cheapest coagulant (alum) dissolution leads to successful green synthesis of nanoparticles of Ca and Al. Precipitation of these particles on the filter sand produces efficient reactive

material that can able to remediate of the groundwater contaminated with methyl orange dye using PRB technique. Results signified that the sorption data can describe by “favorable curve” and Langmuir model is more representative for this curve with  $R^2$  of 0.999 and SSE of 0.0122 where maximum adsorption capacity equal to 0.9453 mg/g and affinity constant of 0.421 L/mg. Desorption results for washing of exhausted coated sand with water proved that only 0.91% of dye can desorb and this reflects the strength of bonding between sorbent and sorbate. Also, the exhausted coated sand can be regenerated with efficiency not less than 85% after eight of regeneration cycles. The longevity (breakthrough time) of coated sand is proportional directly with sorbent quantity (bed depth) and inversely with influent concentration and discharge of flow. The package of COMSOL has a high capability for simulating of breakthrough curves with acceptable matching.

#### REFERENCES

1. Abdulkareem, H. N. and A. I. Alwared, 2019. Immobilization dried mix of algae for copper removal. *Iraqi Journal of Agricultural Sciences*, 50(3),800–808. doi:10.36103/ijas.v50i3.697
2. Abdulkareem, P. M. and S. S. Anwer, 2021. Uptake of different dyes by two new strains of microalgal dry biomass. *Iraqi Journal of Agricultural Sciences*, 52(1),48–62. doi:10.36103/IJAS.V52I1.1235
3. Ahmed, D. N.; L. A. Naji, A. A. H. Faisal, N. Al-Ansari and M. Naushad, 2020. Waste foundry sand/MgFe-layered double hydroxides composite material for efficient removal of Congo red dye from aqueous solution. *Scientific Reports*, 10(1). doi:10.1038/s41598-020-58866-y
4. Alquzweeni, S. S. and A. A. H. Faisal, 2020. Removal of lead ions from aqueous solution using granular iron slag byproduct as permeable reactive barrier. *Iraqi Journal of Agricultural Sciences*, 51(2),723–733. doi:10.36103/ijas.v51i2.1000
5. Ammar, S. H.; H. J. Khadim and A. Al-Farraj, 2020. Synthesis of Ni@ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>@PID\SiW recyclable nanocatalyst and its catalytic reduction and antibacterial activities. *Nanotechnology for Environmental Engineering*, 5(2),1–11. doi:10.1007/s41204-020-00082-0
6. Bo, A.; S. Sarina, H. Liu, Z. Zheng, Q. Xiao, Y. Gu, G. A. Ayoko and H. Zhu, 2016. Efficient removal of cationic and anionic radioactive pollutants from water using hydrotalcite-based getters. *ACS Appl. Mater. Interfaces*, 8(4),16503–16510
7. Chen, Z.; D. Mu, F. Chen and N. Tan, 2019. NiFe<sub>2</sub>O<sub>4</sub>@ nitrogen-doped carbon hollow spheres with highly efficient and recyclable adsorption of tetracycline. *RSC Advances*,. doi:10.1039/c9ra00670b
8. Copaja, S. V.; L. Mauro, C. Vega-Retter and D. Véliz, 2020. Adsorption-desorption of trace elements in sediments of the Maipo river basin. *Journal of the Chilean Chemical Society*, 65(2),4778–4783. doi:10.4067/S0717-97072020000204778
9. Delleur, J. W., 1999. *The Handbook Of Groundwater Engineering*,. Boca Raton: CRC Press. doi:10.5860/choice.pp:36-4507
10. Elmoubarki, R.; F. Mahjoubi, A. Elhalil, H. Tounsadi, M. Abdennouri, M. Sadiqa, S. Qourzal, A. Zouhri and N. Barka, 2017. Ni/Fe and Mg/Fe layered double hydroxides and their calcined derivatives: preparation, characterization and application on textile dyes removal. *Journal of Materials Research and Technology*, 6(3),271–283
11. Faisal, A. A. H.; S. S. Alquzweeni, L. A. Naji and M. Naushad, 2020. Predominant mechanisms in the treatment of wastewater due to interaction of benzaldehyde and iron slag byproduct. *International Journal of Environmental Research and Public Health*, 17(1),226. doi:10.3390/ijerph17010226
12. Faisal, A. A. H.; A. H. Shihab, M. Naushad, T. Ahamad, G. Sharma and K. M. Al-Sheetan, 2021. Green synthesis for novel sorbent of sand coated with (Ca/Al)-layered double hydroxide for the removal of toxic dye from aqueous environment. *Journal of Environmental Chemical Engineering*. 9(4),105342. doi:10.1016/j.jece.2021.105342
13. Fetter, C. W., 1999. *Contaminant Hydrogeology*,. ;2<sup>nd</sup> ed. Prentice-Hall, New Jersey. pp:303
14. Foo, K. Y. and B. H. Hameed, 2010. Insights into the modeling of adsorption isotherm systems, *Chemical engineering journal*, 156(1),2–10

15. Goh, K. H.; T. T. Lim, and Z. Dong, 2008. Application of layered double hydroxides for removal of oxyanions: A review. *Water Research*, 42(7),1343–1368
16. Hamdaoui, O. and E. Naffrechoux, 2007. Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon Part II. Models with more than two parameters. *Journal of Hazardous Materials*, 147(1–2),401–411. doi:10.1016/j.jhazmat.2007.01.023
17. Ho, Y. S.; J. F. Porter and G. McKay, 2002. Equilibrium isotherm studies for the sorption of divalent metal ions onto peat: Copper, nickel and lead single component systems. *Water, Air, and Soil Pollution*, 141(1–4),1–33. doi:10.1023/A:1021304828010
18. Khudhair, E. M.; S. H. Ammar and H. J. Khadim, 2021. Phosphotungstic acid immobilized onto ZnO coated zerovalent iron (Fe@ZnO/PW) core/shell magnetic nanocomposite for enhanced photocatalytic bacterial inactivation under visible light. *Journal of Photochemistry and Photobiology A: Chemistry*, 404(3),112907. doi:10.1016/j.jphotochem.2020.112907
19. Ko, D. C. K.; J. F. Porter and G. McKay, 2000. Optimised correlations for the fixed-bed adsorption of metal ions on bone char. *Chemical Engineering Science*, 55(23),5819–5829. doi:10.1016/S0009-2509(00)00416-4
20. Liang, X.; Y. Zang, Y. Xu, X. Tan, W. Hou, L. Wang and Y. Sun, 2013. Sorption of metal cations on layered double hydroxides. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 433(3),122–131
21. Liao, P.; Z. Zhan, J. Dai, X. Wu, W. Zhang, K. Wang, and S. Yuan, 2013. Adsorption of tetracycline and chloramphenicol in aqueous solutions by bamboo charcoal: A batch and fixed-bed column study, *Chemical Engineering Journal*, 228(12),496–505. doi:10.1016/j.cej.2013.04.118
22. Naji, L. A.; S. H. Jassam, M. J. Yaseen, A. A. H. Faisal and N. Al-Ansari, 2020. Modification of Langmuir model for simulating initial pH and temperature effects on sorption process. *Separation Science and Technology (Philadelphia)*, 55(15),2729–2736. doi:10.1080/01496395.2019.1655055
23. Puls, R. W.; R. M. Powell, D. W. Blowes, J. L. Vogan, R. W. Gillham, P. D. Powell, D. Schultz, T. M. Sivavec and R. Landis, 1998. Permeable reactive barriers technologies for contaminant remediation. United States Environmental Protection Agency, Washington, DC, pp:401
24. Rai, M. K.; G. Shahi, V. Meena, R. Meena, S. Chakraborty, R. S. Singh and B. N. Rai, 2016. Removal of hexavalent chromium Cr (VI) using activated carbon prepared from mango kernel activated with H<sub>3</sub>PO<sub>4</sub>. *Resource-Efficient Technologies*, 2(1),S63–S70. doi:10.1016/j.reffit.2016.11.011
25. Robinson, T.; G. McMullan, R. Marchant and P. Nigam, 2001. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. *Bioresource Technology*, 77(3),247–255. doi:10.1016/S0960-8524(00)00080-8
26. Safarik, I.; L. F. T. Rego, M. Borovska, E. Mosiniewicz-Szablewska, F. Weyda and M. Safarikova, 2007. New magnetically responsive yeast-based biosorbent for the efficient removal of water-soluble dyes. *Enzyme and Microbial Technology*, 40(6),1551–1556. doi:10.1016/j.enzmictec.2006.10.034
27. Sahoo, J. K.; A. Kumar, J. Rath, T. Mohanty, P. Dash and H. Sahoo, 2017. Guar gum-coated iron oxide nanocomposite as an efficient adsorbent for Congo red dye. *desalination and water treatment*, 95(4),342–354. doi:10.5004/dwt.2017.21572
28. Sahoo, J. K.; S. K. Paikra, M. Mishra and H. Sahoo, 2019. Amine functionalized magnetic iron oxide nanoparticles: Synthesis, antibacterial activity and rapid removal of Congo red dye, *Journal of Molecular Liquids*. 282(1),428–440. doi:10.1016/j.molliq.2019.03.033
29. Ujfaludi, L., 1986. Longitudinal dispersion tests in non-uniform porous media, *Hydrological Sciences Journal*, 31(3),467–474
30. Wang, L. and A. Wang, 2007. Adsorption characteristics of Congo Red onto the chitosan/montmorillonite nanocomposite. *Journal of Hazardous Materials*, 147(3),979–985. doi:10.1016/j.jhazmat.2007.01.145
31. Yao, S.; M. Fabbicino, M. Race, A. Ferraro, L. Pontoni, O. Aimone and Y. Chen,

2020. Study of the digestate as an innovative and low-cost adsorbent for the removal of dyes in wastewater. *Processes*, 8(7),852. doi:10.3390/pr8070852

32. Zyoud, A.; A. Zu'bi, M. H. S. Helal, D. Park, G. Campet and H. S. Hilal, 2015.

Optimizing photo-mineralization of aqueous methyl orange by nano-ZnO catalyst under simulated natural conditions. *Journal of Environmental Health Science and Engineering*, 13(1),46. doi:10.1186/s40201-015-0204-0