IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

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To cite this article: S N Ramdzan *et al* 2022 *IOP Conf. Ser.: Earth Environ. Sci.* **1022** 012060

Pre-Treatment of Laundry Greywater by Steel Slag for Safe Disposal

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Abstract. Direct discharge of laundry greywater without any water pre-treatment in the drainage system has become a common practice in Malaysia. The study aimed to utilise steel slag as an adsorbent material for commercial laundry shop runoff (CLSR) to reduce chemical oxygen demand (COD) and total phosphorus (TP). Optimisation of the pollutants removal efficiency in CSLR by steel slag used Response Surface Methodology (RSM) using independent variables; different percentages of CLSR with tap water and contact time. The highest removal efficiency obtained for COD was 54.49% at 100% CLSR with tap water and 60 minutes of contact time. TP removal efficiency was 45.45% at 10% CLSR with tap water and 90 minutes of contact time. Thus, steel slag can increase the pH value, reducing the COD and TP values from CLSR in a short period. Hence, steel slag has the potential to be included in the "pre-treatment" system for CLSR based on its performance at COD and TP removal efficiency. From RSM, the model F-value and P-value for COD and TP were 5.89 and 10.62, 0.0166 and 0.0036, respectively. These values validated that the model was significant. Therefore, the study can contribute to the safe disposal of untreated laundry greywater to minimise environmental degradation.

1. Introduction

The increasing growth of commercial laundry shops, laundromats, or launderettes has brought considerable profits to numerous business owners around the globe in recent years. The impact from this growth of commercial laundry shops in the country will lead to the dark side when the effluents produced from these premises did not undergo "pre-treatment" before being discharged into the surface water. Pre-treatment is the best option for laundry greywater before discharging into the drainage system to reduce the pollutants level in the water body. The high levels of surfactants, phosphates, and other organic matters in commercial laundry shop runoff will eventually enhance the levels of COD in waterways. Steel slag, a by-product of the steel-making process that serves no other purpose in the upcoming steel production process, with the main components of SiO_2, CaO, and Fe_2O_3 [1] are proven to lower COD levels at the average removal rate of more than 70% by releasing oxide minerals to bind with organic matter in wastewater [2]. However, there are no previous studies regarding the removal of COD that can affect the steel slag's ability to remove organic matter and the removal mechanism. Thus, the utilisation of steel slag as an adsorptive material would offer insights about this issue to reduce the levels of contaminants in commercial laundry shop runoff (CLSR) to protect the environment simultaneously.

Consequently, the use of laundry detergents has increased along with the growth of laundromats. The need to fulfil customer demands has always been the primary concern towards laundromats. These services are often addressed through a personal approach [3]. Advance techniques and technologies are applied to various types of fabrics, such as dyeing, bleaching, and starching using various chemicals in order to remove any smear and dirt from the fabrics [4]. Table 1 shows the types of detergents used for laundry purposes and their characteristics.

Table 1. Types and properties of laundry detergent

Types of Detergent	Characteristic	Functionality
Phosphate Detergent	• Contains phosphate • Corrosive	• Soften hard water • Suspend dirt
Surfactant Detergent	• Contains surfactant • Toxic in nature	• Enhance foaming wetting and dispersing • Emulsifying detergent’s properties

From Table 1, phosphate acts as a builder in the form of sodium pyrophosphate and sodium tripolyphosphate. It will nourish the microorganisms and cause eutrophication [5]. The presence of surfactants in detergent enhances the performance of detergent by acting as an emulsifier for detergent’s properties and enhancing the foaming wetting and dispersions. Both detergents lead to water pollution due to the corrosive nature of phosphate and the toxicity of surfactants in nature.

The chemical composition of steel slag that contains high calcium ion and magnesium ion, the pH value of water would increase. The hydration of steel slag composition causes an increase in pH value in the water sample from 6.3 to 8.3 [6]. Calcium silicates, magnesium oxide, calcium aluminates, and calcium oxide are responsible for the major hydration reaction in the water sample [6]. These reactions are shown in Equations (1)–(4).

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{1}$$

$$\mathrm{CaO} + \mathrm{H_2O} \rightarrow \mathrm{Ca(OH)_2} \tag{2}$$

$$\mathrm{2Ca_3SiO_5} + \mathrm{6H_2O} \rightarrow \mathrm{3CaO\,.\,2SiO_2\,.\,3H_2O} + \mathrm{3\ Ca(OH)_2} \tag{3}$$

$$\mathrm{CaO\,.\,7Al_2O_3} + \mathrm{12H_2O} \rightarrow \mathrm{CaO\,.\,Al_2O_3\,.\,6H_2O} + \mathrm{6Al_2O_3\,.\,H_2O} \tag{4}$$

Steel slag has the potential to decrease the value of COD through the ions contained in the steel slag. The oxide minerals such as calcium oxide and magnesium oxide discharged from the steel slag are the main factors contributing to the COD removal of wastewater [2]. The mechanism of COD removal was proved to be caused by an ion reaction. The organic matter in the water sample was adsorbed by the oxide mineral of calcium oxide and magnesium oxide discharged from the steel slag and precipitated the matter [2]. The efficiency of steel slag to lower the value of COD was proved by Huang et al. [7], who utilised steel slag as wetland substrate, giving the removal rate of COD on average was more than 70%.

The process of COD removal using steel slag cannot determine the steel slag’s capabilities for the removal mechanism and the types of organic matter’s removal through various experiments. This is because COD is used to indicate the presence of organic pollutants in the water [8]. The increase in the initial phosphorus concentration in water increases the amount of adsorption until the equilibrium state is achieved as the quantity for sediment adsorption per unit mass is enhanced by the increase of the initial phosphorus concentration in water under the state of quasi-equilibrium [9].

Thus, phosphorus removal can be enhanced using a higher initial concentration of CLSR in the water samples. The results for the phosphate removal rate increased linearly to the contact time [10]. Approximately 85% of phosphorus removal was achieved with the increase in contact time [11]. The longer the contact time, the higher the phosphorus removal before it reaches an equilibrium where there is no phosphorus removal beyond a certain duration.

The high percentage of steel slag will contribute to the high composition of free calcium (CaO) that helps in the phosphate removal from laundry greywater. Phosphorus can be removed through phosphorus precipitation with the presence of free calcium (CaO) and produce the compound of calcium phosphate ($\mathrm{Ca_3(PO_4)_2}$) [8]. The mechanism of phosphorus precipitation is shown in Equations (5) and

(6). A similar reaction also had been discovered by Vohla et al. [12], who produced hydroxyapatite precipitation from the free calcium in common slags such as electric arc furnace slag (EAFS), blast furnace slag (BSFS), and basic oxygen furnace slag (BOFS) with phosphate in the high pH value of water sample. The process of hydroxyapatite precipitation is shown in Equations (7) and (8).

$$\mathrm{CaO + H_2O \rightarrow Ca^{2+} + H_2O_2} \tag{5}$$

$$\mathrm{Ca^{2+} + PO_4{}^{3-} \rightarrow Ca_3(PO_4)_2} \tag{6}$$

$$\mathrm{CaO + H_2O \rightarrow Ca^{2+} + 2OH^-} \tag{7}$$

$$\mathrm{5Ca^{2+} + 3PO_4{}^{3-} + OH^- \rightarrow Ca_5(PO_4)_3(OH)} \tag{8}$$

The composition of metal oxides such as alumina ($\mathrm{Al_2O_3}$) and hematite ($\mathrm{Fe_2O_3}$) exist to enable the steel slag to reduce phosphorus from municipal and domestic effluents [13]. The presence of iron (Fe), aluminium (Al), and calcium (Ca) oxides in fly ash makes it a competent material for phosphorus adsorption [14]. Thus, steel slag is a competent material for phosphorus adsorption as iron (III) oxide ($\mathrm{Fe_2O_3}$), aluminium oxide ($\mathrm{Al_2O_3}$) and calcium oxide (CaO). The accumulation of hydroxyapatite ($\mathrm{Ca_5(PO_4)_3(OH)}$ found at the surface of iron oxide, such as hematite, through SEM analysis and XRF analysis. The differences in physicochemical property create a broad phosphorus adsorption capacity, which is between 76.4 mg/kg to 8390 mg/kg [13]. Therefore, there is potential for phosphate removal in CLSR from using steel slag as adsorptive material in CLSR. The objectives of the study are to characterise the pH, concentration of COD, and TP from commercial laundry shop runoff and identify the properties of steel slag and evaluate the influence of steel slag on CLSR by optimising CLSR percentage with tap water and contact time using RSM.

2. Materials and methods

CLSR samples were collected at the Dobi Al-Hijrah in Batu Pahat, Johor. Samples were collected on weekdays (Monday and Wednesday) and weekends (Sunday) at 9:00 a.m. because it is the ideal time to collect the sample and conduct the parameter testing for the raw water samples where the parameter of pH needs to be tested in 15 minutes [15]. CLSR samples were taken immediately after the wash phase as the effluent after that phase contains more detergent than the rinse phase through the hose of the washing machine.

Samples were stored in high-density polyethylene (HDPE) container (Figure 1) to prevent the leakage of CLSR from the container due to its durability, strength, and resistance to many chemicals; hence its widespread use in laboratory environments. The collected samples were transferred to Pusat Penyelidikan Pencemar Mikro (MPRC) in the Faculty of Civil Engineering and Built Environment (FKAAB) with the implementation of several precautionary steps. Table 2 shows the requirements for the sample preservation method and holding time. Then, several tests were conducted on the samples to identify the value for pH, COD, and TP for the water samples of raw CLSR and treated CLSR.

Samples of steel slag were taken from the quarry located in Pasir Gudang, Johor. All the samples were stored in the black bin as it is convenient and able to sustain the heavy weight of the steel slag. Figure 2 shows the heaps of steel slag in the quarry. The collected samples of steel slag were washed initially to remove the dirt with tap water and left to dry under the sun until the steel slag was completely dried for 4 to 5 hours, depending on the current weather. The size range of steel slag used was 0.5–3.0 cm. Figure 3 shows the washed steel slag dried under the sun.

Figure 1. The CLSR sample in the container

Table 2. Sample preservation and holding time requirements (APHA, 2012)

No.	Parameter	Sample Container	Storage Temperature (°C)	Preservation	Holding Time
1	pH	Plastic	≤ 6	None	15 minutes
2	COD	Plastic	≤ 6	H_2SO_4 (field or lab)	28 days
3	TP	Plastic	≤ 6	H_2SO_4	28 days

COD: Chemical Oxygen Demand, TP: Total Phosphorus, H_2SO_4: sulphuric acid

Figure 2. The heaps of steel slag

Figure 3. The drying of steel slag under the sun

Figure 4 shows the mechanism of incorporating steel slag and CLSR to observe the steel slag's direct effect on CLSR along with the implementation of optimisation factors for RSM. The experimental data were analysed as removal efficiency for pH, COD, and TP.

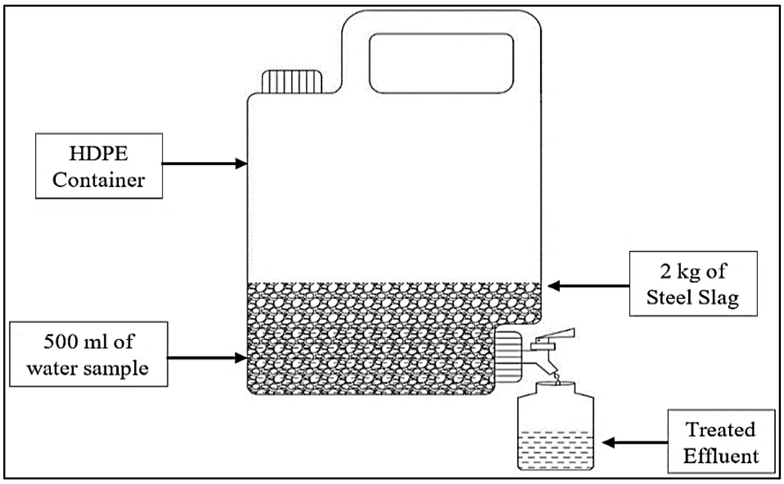

Figure 4. The mechanism of incorporating steel slag with CLSR

3. Results and Discussion

The chemical characteristics of steel slag were characterised through X-ray Fluorescence Spectroscopy (XRF) analysis (Table 3). Elements play an important role as the adsorbent element for phosphorus adsorption, such as CaO. The dissolution of free calcium (CaO) will increase with the higher content of free calcium to remove phosphorus through the calcium-phosphate precipitation [16].

Table 3. Chemical composition of steel slag based on XRF analysis

No.	Element	Percentage (%)
1	SiO_2	32.294
2	CaO	30.217
3	Fe_2O_3	12.963
4	MgO	11.173
5	Al_2O_3	7.897
6	Mn_2O_3	1.687
7	SO_3	0.975
8	Na_2O	0.955
9	ZnO	0.636
10	K_2O	0.383
11	Cr_2O_3	0.376
12	TiO_2	0.289
13	Cl	0.079
14	P_2O_5	0.075

Table 4 shows the physicochemical characteristics for COD and TP values of the collected CLSR at different percentages of CLSR with tap water. The pH value for all percentages of CLSR with tap water does not comply with Standard B, but all the values for COD have complied with Standard B. The value for TP was within Standard B at 10%. The standard effluent level is implemented and compared to treat CLSR as there is no regulation imposed yet on laundry greywater effluent discharge in Malaysia [17].

Table 4. Mean ± standard deviation characteristics of the raw samples of CLSR, n = 3 samples

Sample	Percentage of CLSR with Tap Water (%)	COD (mg/L)	Total P (mg/L)
Standard Effluent (Standard B)	-	200	10.00
A	100	156	14.67

B	55	77	13.12
C	10	21	9.88
Mean ± Standard Deviation		84.67 ± 67.83	12.56 ± 2.44

CLSR: Commercial Laundry Shop Runoff, COD: Chemical Oxygen Demand, P: phosphate/phosphorus

Based on Table 5, the steel slag filter achieved the highest removal efficiency of COD which is 54.49% with 100% of CLSR with tap water and 60 minutes of contact time. Each sample of the treated CLSR was found to vary in the percentage of CLSR (10–100%) with tap water with the allocated contact time (30–90 min) in the optimisation factors for RSM. The container used for the 2 kg of steel slag reacts with 500 mL of CLSR based on the specific percentage of CLSR with tap water. The discharged oxide minerals such as calcium oxide and magnesium oxide from the steel slag are the main factors that contribute to the COD removal of wastewater [2]. The COD concentration of all the treated CLSR effluent was met and complied with the required COD concentration for laundry effluent based on Standard B, which is lower than 200 mg/L. The highest COD value for the treated CLSR of 97.0 mg/L is safer to be discharged because it contains lower organic and inorganic constituents than the water sample of CLSR.

Steel slag filter had achieved the highest removal efficiency of TP, which is 45.45% with 10% of CLSR with tap water and 90 minutes of contact time. The lowest COD removal efficiency is 3.00% with 100% CLSR with tap water and 30 minutes of contact time as factors. The TP concentration for the treated CLSR was increased from 14.67 mg/L to 14.23 mg/L, only reducing the low concentration of TP. A high concentration of CLSR might hinder the steel slag's adsorption capacity in a short amount of time, 30 minutes. This can be seen when there is a significant reduction at 30 minutes in TP concentration at 55% and 10% of CLSR with tap water, which are 3.52 mg/L and 2.78 mg/L, respectively, but only slightly reduced, which is 0.44 mg/L at 100%. The increase in the initial phosphorus concentration in water increases the amount of adsorption until the equilibrium state is achieved as the quantity for sediment adsorption per unit mass is enhanced by the increase of the initial phosphorus concentration in water under the state of quasi-equilibrium [9].

However, the adsorption of phosphate increases linearly with the contact time. It reaches equilibrium after the specific duration based on its initial phosphate concentration [18]. TP concentration of the 4 samples out of 13 the treated CLSR effluent at 55% (30 minutes) and 10% of CLSR with tap water complies with the required TP concentration for laundry effluent based on the Standard B which is lower than 10 mg/L as the lowest TP value for treated CLSR is 5.39 mg/L. Only 4 samples of the 13 samples tested had a total P level that met the effluent standard. Hence, the adsorption reaction is more effective when the CLSR percentage is low (10%) and performed in a short period (30 min).

Table 5. Steel slag's removal efficiency on CLSR

No.	Percentage of CLSR with Tap Water (%)	Contact Time (min)	Removal Efficiency (%)	
			COD	**TP**
1	100	90	37.82	8.11
2	100	60	**54.49**	4.02
3	100	30	48.29	**3.00**
4	55	90	15.58	21.95
5	55	60	51.52	7.32
6	55	60	27.70	12.96
7	55	60	6.49	6.55
8	55	60	27.27	5.87
9	55	60	28.57	8.54
10	55	30	24.68	26.83
11	10	90	7.95	**45.45**
12	10	60	22.24	34.51
13	10	30	**-166.67**	28.14

CLSR: Commercial Laundry Shop Runoff, COD: Chemical Oxygen Demand, P: phosphate/phosphorus

Table 6 shows the optimal condition for COD and TP removal efficiency using steel slag as adsorptive material compatible with the predicted value generated from the RSM (Design Expert). The difference in the removal percentage values of COD and TP between the predicted value and actual value programmed by RSM are lower than the standard error of 5%, indicating that this model of study is significant and applicable. The higher removal of COD value than TP value in raw water samples indicates a higher level of organic matter other than TP.

Table 6. Optimal operating conditions for COD and TP removal efficiency.

No.	CLSR with Tap Water (%)	Immersion Time (min)	COD (mg/L)			TP (mg/L)		
			Initial	Final	Removal (%)	Initial	Final	Removal (%)
1	100	90	-	-	40.051	-	-	9.307
2	100	90	369.67	228.33	38.234	11.09	10.60	4.89

CLSR: Commercial Laundry Shop Runoff, COD: Chemical Oxygen Demand, P: Phosphate/Phosphorus

The data analysed by RSM through Design Expert software for COD and TP removal efficiency is shown in Figure 5 and Figure 6, respectively.

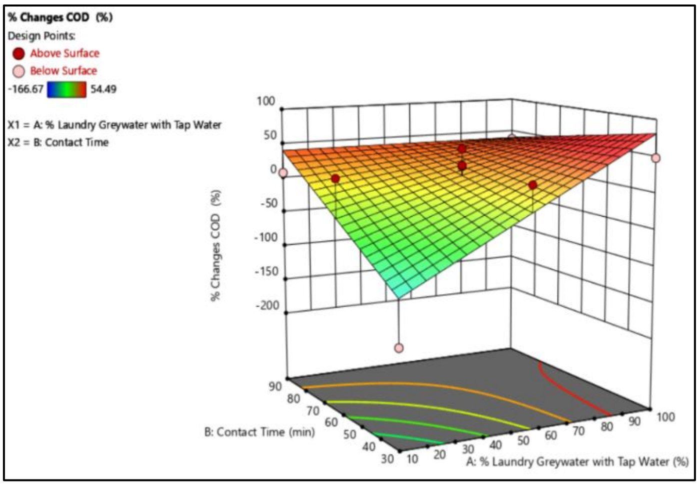

Figure 5. Design expert plot, 3D surface graph COD

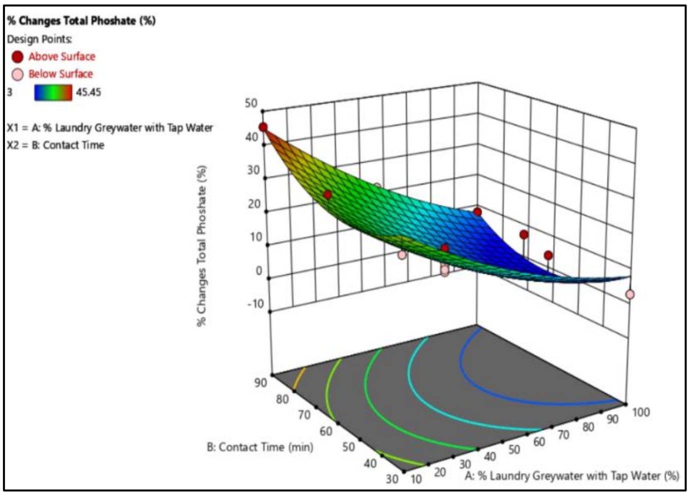

Figure 6. Design expert plot, 3D surface graph TP

4. Conclusion

XRF analysis revealed high percentage of CaO (30.217%) and MgO (11.173%) in steel slag. The pH, concentration of COD, and TP from CLSR were 10.58, 156 mg/L and 14.67 mg/L, respectively. The influence of steel slag on CLSR was evaluated by optimising the percentage CLSR with tap water and contact time using RSM. Steel slag had the highest removal efficiency of COD (54.49%) at 100% CLSR with tap water and 60 minutes of contact time. Steel slag works best for TP removal efficiency of 45.45% at 10% CLSR with tap water and 90 minutes of contact time. It is suggested to measure hydraulic retention time (HRT) as one of the optimisation factors for RSM and incorporate steel slag with the permeable concrete mixture for a more detailed study on the removal mechanism.

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Acknowledgments

The authors would like to thank the Ministry of Higher Education Malaysia (MOHE) for providing the Fundamental Research Grant Scheme (FRGS) with reference code: FRGS/1/2019/WAB05/UTHM/02/5 (Modification of Bead Adsorbents with Ceramic Sanitary Ware Waste (CSWW) and Chitosan for Laundry Greywater (LGW) Safe Disposal) and the Research Management Centre (RMC), UTHM for providing the GPPS Grant vot H637 (Inactivation of Antibiotic-Resistant Bacteria in Prawn Farm Wastewater using ZnO NPs Biosynthesized) as financial support for this research.