Removal of antibiotics (sulfamethazine, tetracycline and chloramphenicol) from aqueous solution by raw and nitrogen plasma modified steel shavings

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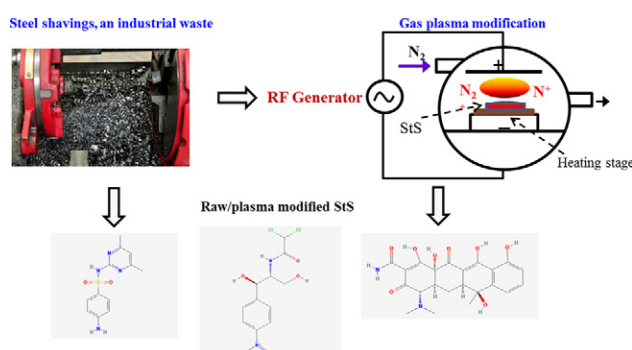[c] State Key Laboratory of Hollow Fiber Membrane Materials and Processes, School of Materials Science and Engineering, Tianjin Polytechnic University, Tianjin 300387, PR China
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HIGHLIGHTS

- Both raw and nitrogen plasma modified StS can remove antibiotics from water.
- N_2 plasma improved 1.7-fold the surface area and 1.4-fold the pore volume of StS.
- Solution pH has a great influence on adsorption capacity.
- Sorption is mostly governed by H-bonds, electrostatic & non-electrostatic, redox.
- Main components of StS's surface: Fe_3O_4/Fe^{2+}, Fe_3O_4/Fe^{3+}, FeO/Fe^{2+} and Fe_2O_3/Fe^{3+}.

GRAPHICAL ABSTRACT

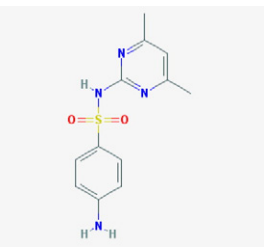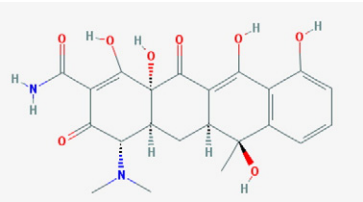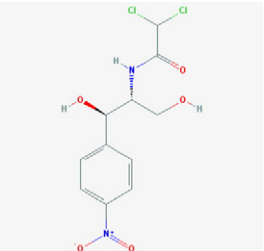## ARTICLE INFO

ABSTRACT

The removal of sulfamethazine (SMT), tetracycline (TC) and chloramphenicol (CP) from synthetic wastewater by raw (M_3) and nitrogen plasma modified steel shavings (M_3-plN$_2$) was investigated using batch experiments. The adsorption kinetics could be expressed by both pseudo-first-order kinetic (PFO) and pseudo-second-order kinetic (PSO) models, where correlation coefficient r^2 values were high. The values of PFO rate constant k_{1p} and PSO rate constant k_{2p} decreased as SMT-M_3 > SMT-M_3-plN$_2$ > TC-M_3-plN$_2$ > TC-M_3 > CP-M_3 > CP-M_3-plN$_2$ and SMT-M_3 > SMT-M_3-plN$_2$ > TC-M_3 > TC-M_3-plN$_2$ > CP-M_3 > CP-M_3-plN$_2$, respectively. Solution pH, adsorbent dose and temperature exerted great influences on the adsorption process. The plasma modification with nitrogen gas cleaned and enhanced 1.7-fold the surface area and 1.4-fold the pore volume of steel shavings. Consequently, the removal capacity of SMT, TC, CP on the adsorbent rose from 2519.98 to 2702.55, 1720.20 to 2158.36, and 2772.81 to 2920.11 μg/g, respectively. Typical chemical states of iron (XPS in Fe2p3 region) in the adsorbents which are mainly responsible for removing antibiotics through hydrogen bonding, electrostatic and non- electrostatic interactions and redox reaction were as follows: Fe_3O_4/Fe^{2+}, Fe_3O_4/Fe^{3+}, FeO/Fe^{2+} and Fe_2O_3/Fe^{3+}.

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Table 1
Chemical structure and properties of the study antibiotics (Ahmed et al., 2015; Adams et al., 2002; Homem and Santos, 2011; Xia et al., 2014; Pubchem, 2017).

Compound, CAS number	Molecular formular, weight	Logkow, pKa, Solubility	Analysis wave length	Possible structure	Core structure	Treatment methods
Sulfamethazine 57-68-1	$C_{12}H_{14}N_4O_2S$ 278.34	0.14/0.28 2.65/7.65 $4.3(10^2)$	275		It is characterized by sulfonyl group connected to an amine group	Coagulation, flocculation, sedimentation, excess lime, soda ash, softening, powdered activated carbon sorption, chlorination, ozonation, direct photolysis, ion exchange, reverse osmosis, nanofiltration, semiconductor photocatalysis, photo-fenton
Tetracycline 60-54-8	$C_{22}H_{24}N_2O_8 \cdot HCl$ 444.43	−1.37 3.3 8.3	260		This antibiotic contains an octrahydronaphtacene ring skeleton, consisting of 4 fused rings	Ion exchange, nanofiltration, coagulation, adsorption with activated carbon, adsorption with aluminum oxide, semiconductor photocatalysis, photo-fenton, direct photolysis
Chloramphenicol 56-75-7	$C_{12}H_{12}Cl_2N_2O_5$ 323.13	$1.14–5.5^2$	272/278		It contains a nitrobenzene moiety connected to a propanol group as well as an amino group binding a derivative of dichloroacetic acid	Semiconductor photocatalysis, nano zero-valent iron, adsorption, advanced oxidation

1. Introduction

Water pollution by antibiotics has become a widespread environmental problem (Homem and Santos, 2011). The chemicals are
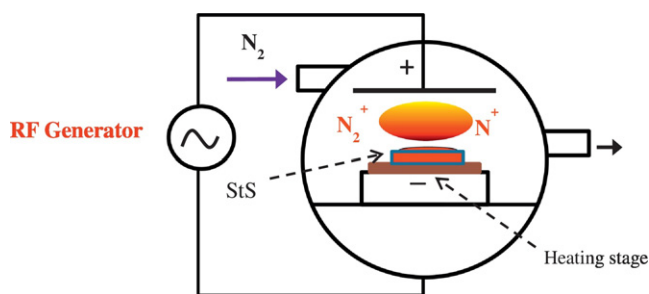

Fig. 1. Radio frequency (RF) plasma configuration for the surface treatment of StS.

expansively used in human and veterinary medicine for inhibiting illness (Sapkota et al., 2008). Recent studies have shown that a number of antibiotics are detected in surface and groundwater (Homem and Santos, 2011). Most antibiotics enter the environment, notably in the aquatic matrix, through discharge or disposal from medical, municipal, and agricultural sources (Daughton and Ternes, 1999; Sapkota et al., 2008). Even low concentrations of antibiotics in water can pose serious problems to the ecosystem such as their potential risks of environmental toxicity and promote microbial resistance (Ahmed et al., 2015; Homem and Santos, 2011).

Some typical antibiotics were selected in the present study including sulfamethazine (SMT), tetracycline (TC) and chloramphenicol (CP). SMT is a compound belonging to the sulphonamide group. SMT is usually used in veterinary medicine or livestock feeds for cattle and swine, and can be detected at high concentration in aqueous solution due to soil's poor ability to adsorb it (Aust et al., 2010; Wegst-Uhrich et al., 2014). TC, which belongs to the tetracyclines group of antibiotics, is also applied to livestock as additives to combat diseases (Chen et al.,

Table 2
Kinetic and isotherm models of antibiotics adsorption on StS.

Models	Equation	Linearized form
Langmuir	$q_e = \frac{q_{max}k_L C_e}{1+k_L C_e}$	$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{k_L q_{max}}$
Freundlich	$q_e = k_F C_e^{1/n}$	$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e$
	where: C_e is the equilibrium concentration of the adsorbate (µg/L). q_e is adsorption capacity of StS at equilibrium (µg/g). q_{max} is maximum antibiotics uptake of the adsorbent (µg/g); k_L is Langmuir constant related to binding energy of adsorption (L/µg); k_F and n are Freundlich constants indicative of the adsorption capacity and adsorption intensity of the adsorbent, respectively.	
PFO	$\frac{dq_t}{dt} = k_{1p}(q_e - q_t)$	$\ln(q_e - q_t) = \ln q_e - k_1 t$
PSO	$\frac{dq_t}{dt} = k_{2p}(q_e - q_t)^2$	$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}$
IDM	$q_t = k_i t^{0.5}$	
	where: qe = amount of antibiotics adsorbed at equilibrium (µg/g); qt = amount of antibiotics adsorbed at time t (min) (µg/g); k_{1p} = equilibrium rate constant of PFO (1/min); k_{2p} = equilibrium rate constant of PSO (1/min) and ki (µg/g min) = the rate constants of IDM, respectively.	